A STUDY OF SLAG-METAL EQUILIBRIA IN STEEL MAKING PRACTICE WITH SPECIAL REFERENCE TO SULPHUR.

THESIS PRESENTED

BY

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OCTOBER, 1949.

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CHAPTER I.

One of the most important functions of the basic open-hearth furnace is to reduce the sulphur content of the metal charge to below the specification set by the use to which the steel is going to be put.

The sulphur is introduced into the furnace as that contained in the metal, the slag-making additions and also as that contained in the fuel gases. It should be noted that the sulphur contained in the gases is several times that introduced with the solid charge.

It has long been recognised that the chemical composition of the slag is the main factor in sulphur removal in the basic open-hearth process, although its physical condition also plays a prominent part. It is an established fact that the lime content of the slag is of major importance in sulphur removal. This factor has been expressed in various ways, the term most widely used being that of "basicity", although there is no agreed method for the assessment of this term. It has been defined as the value of "free lime" existing in the slag, and its calculation has been based on the assumption of the existence of certain molecular species in the liquid slag, any lime in excess of the amount required for the formation of these compounds defining the "basicity" of the slag.

Recently, Grant and Chipman [1] put forward the hypothesis that/

that the action of a basic slag in sulphur removal is not chemical but physical. Their experimental results seem to indicate that the classic reaction to which sulphur removal by basic slag has long been attributed, i.e.

$$FeS + CaO = FeO + CaS$$

is not of any appreciable importance in the basic open-hearth slag. They state that iron sulphide distributes itself between the metal and slag and that the more basic the slag the more FeS it will take into solution.

Lately, Temkin [2] has put forward the theory that liquid slags behave as electrolytes, and proceeded, with Samarin and Shvarzman [3], to explain desulphurisation according to the electrolytic theory of slags. They applied it to slag-metal systems prepared and studied by several workers, and their results are very encouraging.

It was not until recent years that any attempt was made to explore the possible effect the sulphur content of the furnace gases might have on the desulphurising action in the open-hearth process.

In 1923, Whiteley [4] was probably among the first to establish the fact that the sulphur content of the gases did have a considerable bearing on the sulphur content of the bath. In his investigations on an acid open-hearth furnace/

furnace he found out that considerable sulphur pick-up occurred during the melting-down of the metal when the gases were incompletely burnt, while comparatively little sulphur pick-up, if any, occurred if there was excess air in the flame. In some cases where excess air was admitted through the port, desulphurisation of the scrap occurred to a certain extent. His investigation on the transfer of sulphur from gas to bath or vice versa, after a slag was formed, seemed to indicate a definite loss of sulphur from the slag and metal globules contained therein to the gas when air only was passed through the furnace for twenty minutes during the boiling period, but failed to show that the reverse occurred when air was completely cut off and the producer gas allowed to pass over the bath for a similar period of time. The explanation put forward by Whiteley was that there was a limit to the sulphur that could be carried by an acid slag, beyond which no further sulphur pick-up was possible.

This investigation by Whiteley was followed by a number of similar investigations and experiments in the few years that followed.

The investigations of Nead [5], Herty and co-workers [6] [7] [8], Jung [9], Hibbard [10], Geiger [11], Dahlström and Ahren [12],/

Ahren [12], Köhler [13], Diehl [14] and Eisenstecken and Schulz [15] prove beyond doubt that under certain conditions considerable amounts of sulphur could be introduced into the metal from the furnace gases. They all agree on the following conclusions:-

1. The most critical stage in the operation of the open-hearth process for sulphur pick-up from the gases is the melting-down stage, especially if light scrap constitutes part of the charge.

2. The amount of sulphur transferred from gas to metal is directly proportional to the sulphur content of the furnace gases and, therefore, of the fuel used.

3. If very low sulphur fuel or sulphur-free fuel is used desulphurisation of the scrap may take place. This depends, however, on the relative sulphur contents of the scrap and gas.

4. The best way to minimise sulphur pick-up is to shorten the melting-down period to a minimum by using a hot flame, and to use a low sulphur fuel whenever possible.

There was, however, disagreement on whether sulphur moved from gas to slag or vice versa, once the melting-down period was over and a slag formed. Herty [6], Köhler [13] and Diehl [14] favoured the former view while Meyer and Görrissen [16], Dahlström and Ahren [12] and Whiteley [4] favoured the latter. Of all the investigations mentioned

above/

above, the most outstanding were those carried out by Herty and co-workers [6] [7] [8] and by Diehl [14].

Herty was the first to attempt a quantitative approach to the problem of sulphur pick-up from the furnace atmosphere. He assumed the sulphur in the gas to be present as sulphur dioxide and attributed the sulphur pick-up by the melting iron to either or both the following reactions:-

$$SO_2 + 3Fe = FeS + 2FeO \qquad (1)$$

$$3SO_2 + 7Fe = 3FeS + 2Fe_2O_3 \qquad (2)$$

He worked out the distribution ratio of sulphur between the gas and iron oxides thus formed in his experiments as being:-

$$\frac{\text{Vol. \% } SO_2 \text{ in gas over bath}}{\text{\% S in oxide drippings}} = 0.90$$

His statement that the melting iron will be saturated with iron oxide is quite plausible, but that its sulphur content will be the same as that of the oxide drippings is most improbable. Since the sampling procedure is not regarded as satisfactory by the author, it could well account for such a statement.

He gave the following equations to explain the reaction between sulphur dioxide and slags containing lime:-

$$SO_2 + 3CO + CaO = CaS + 3CO_2 \qquad (3)$$

and $$SO_2 + CaO + 3Fe = CaS + 3FeO \qquad (4)$$

The CO taking part in reaction (3) is derived from the reaction/

reaction between the oxygen and carbon in the bath and, according to Herty, has nothing to do with CO in the furnace atmosphere. In reaction (4) iron is in the vapour state and is assumed to be present at all times in the slag. Herty gives the ratio in this case as being:-

$$\frac{\text{Vol. \% } SO_2 \text{ in gas over bath}}{\text{\% S in slag}} = 0.27$$

The ratios given above are purely empirical and are obviously of little or no thermodynamic significance, since in his treatment of the problem Herty does not take into consideration either the effect of temperature or the effect of the state of oxidation of the flame, i.e. the ratio CO : CO_2 prevailing in the furnace atmosphere, or that of the slag. Obviously, in all his experiments the flame was highly oxidising. It is, however, significant that in both reactions (3) and (4) the need of a reductant (CO in (3) and Fe in (4) is essential if sulphur is to pass from the gas to the slag.

Diehl [14], was probably the first to construct a sulphur balance for the open-hearth furnace which took into account the sulphur carried in and out of the furnace with the gases. In addition, he carried out experiments on the sulphur pick-up by scrap and iron bars during the melting stage, by steel ingots in soaking pits, and by liquid slags under oxidising and reducing conditions. His results can/

Fig. 1.— Effect of Mixture of By-Product and Natural Gases on Percentage of Heats Finishing over 0.040% S.

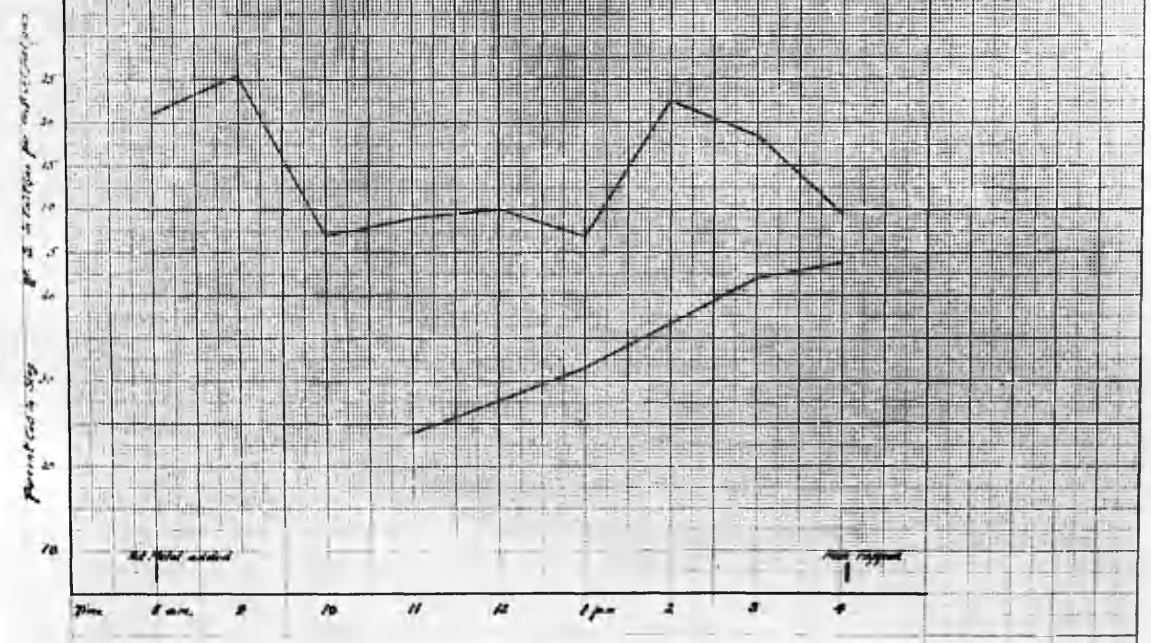


Fig. 2.— Sulphur in Steel Coil with Natural Gas as Fuel

can be summarised as follows:-

1. In all cases sulphur will be absorbed from furnace gases containing sulphur when combustion is incomplete. On the other hand, sulphur will be lost to the furnace gases, even when they contain sulphur, when combustion is complete.

2. In all the 20 open-hearth heats studied, less sulphur left the furnace in the slag and steel than was charged into the furnace with the solid materials. This indicated that some sulphur left the furnace with the waste gases. This was confirmed by the analysis of the sulphur content of the waste gases. This is illustrated in Fig. (2), taken from Diehl's work.

3. The sulphur content of the finished steel was greatly influenced by the sulphur content of the gas. This is well illustrated in Fig. (1), also taken from Diehl's work.

4. The sulphur is removed from the slag by the direct oxidation of CaS into CaO and SO_2.

5. If fuel free from sulphur is not available it becomes extremely important that the gas be burned so as to oxidise the hydrogen sulphide before coming in contact with the scrap, metal or slag.

6. During an average 60 tons heat in an open-hearth furnace, 343 lbs. of sulphur will be carried through the/

the furnace by coke-oven gas and 225 lbs. with producer gas. This means that if a small fraction of the sulphur carried through the furnace with the gases were absorbed by the bath, the melt would be spoilt.

Although the investigations described so far fail to establish any of the fundamental reactions responsible for the absorption of sulphur from the gases in the open-hearth furnace with any certainty, they indicate two important points which were followed up by subsequent workers:-

1. If the conditions prevailing in the open-hearth furnace lead to the absorption of sulphur from the furnace gases, the bulk of the sulphur thus absorbed occurs during the melting down period.

2. The most important factor affecting sulphur absorption from the furnace gases by the melting iron seems to be the state of combustion of the fuel.

At this point the reactions taking place between the sulphur in the gas and the bath in the open-hearth furnace could be grouped as follows:-

(a) Gas-metal reactions, mainly during the melting-down period and to a larger extent during the boil when droplets of liquid iron are projected into the furnace atmosphere.

(b) Gas-slag reactions. These will come into operation as soon as a slag is formed.

Maurer and Bischof [17], in 1934, were the first to investigate, experimentally, the physico-chemical principles underlying the reactions taking place between the sulphur of the gas and liquid iron in the open-hearth furnace. They gave the fundamental sulphur reactions as being:-

$$Fe_{(liq.)} + H_2S = \underset{(metal)}{FeS} + H_2 \qquad (5)$$

$$Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2 \qquad (6)$$

They carried out their experiments in a Tamman furnace and later in a high-frequency furnace. A gas of known initial composition was made to circulate continuously in the space above a charge of molten steel in a closed crucible. At the end of a definite period a sample of the gas was drawn off and analysed. This gave the direction in which the movement towards equilibrium was taking place. This procedure was used to determine the exact position of equilibrium at a given temperature, since they found it impossible to prolong the time of reaction to the point of complete equilibrium. They carried out their determinations at two temperatures for both reactions (5) and (6) and their results are given by:

$$\log \frac{H_2S}{H_2 \cdot S_{(metal)}} = -\frac{693.1}{T} + 0.2447 \qquad (7)$$

and/

and

$$\log \frac{SO_2}{O_2 \cdot S_{(metal)}} = - \frac{1730}{T} + 0.3027 \qquad (8)$$

Maurer and Bischof's results indicated direct proportionality between the sulphur content of liquid iron and the ratios $SO_2 \cdot O_2$ and $H_2S : H_2$. They also showed that the law of mass action was applicable in these two reactions in its ideal form only at low sulphur concentrations in the metal. With an increasing sulphur content in the metal there was a distinct divergence from the operation of the so-called ideal law of mass action, since the reaction constant, in both cases, increased considerably with an increasing sulphur content of the metal. This conclusion is to be expected, since the solubility of FeS in liquid departs from ideality as the sulphur content of the iron increases and a tendency towards separation develops in the system liq. Fe - FeS.

This has been predicted by Bardenheuer and Geller (18) on their examination of the phase diagram Fe - FeS according to Loebe and Becker.

In the second part of their work, Maurer and Bischof proceeded to derive "a law applicable to the behaviour of the sulphur in the open-hearth furnace". They made use of the data recorded by Diehl, especially those dealing with the/

the composition of the fuel gas, waste gas and sulphur content of the steel. By plotting the percentage of sulphur in steel against the ratios S_p/H_2 and S_E/O_2 (S_p being the sulphur in gms/cu.m. in the fuel gas and S_E the sulphur in gms/cu.m. in the waste gas) and by denoting the points with an arrow to indicate the direction in which the sulphur in the steel was moving, two diagrams were obtained. From these two diagrams they concluded that there was no clear connection between the values of S_p/H_2 and the sulphur content of the steel, whereas a comparatively narrow divergence was obtained when ratios of S_E/O_2 were plotted against the sulphur content of the steel. This afforded a clear proof that in the desulphurisation of steel the ratio $SO_2 : O_2$ or $S_E : O_2$ was the decisive factor.

Pursuing their theoretical treatment of the significance of the composition of the fuel gas with regard to the behaviour of the sulphur, Maurer and Bischof stressed the importance of excess air in the furnace gases and stated that it is possible to improve the conditions of desulphurisation by the continuous control of the CO_2 & O_2 contents of the waste gas.

Maurer and Bischof's experimental work and deductions are open to serious objections. Chipman and Ta Li [19] criticised the validity of equation (6) and stated that it/

it was thermodynamically unsound. This criticism will be dealt with later. Another serious deficiency in their treatment of the problem is their complete disregard of the composition of the slag, in the open-hearth heats studied by Diehl, and its bearing on the movement of sulphur between gas and bath, especially its "free" lime content.

Schenck [20], made an attempt to determine the sulphur content of those gases which, in regard to the sulphur reaction are in equilibrium with liquid iron. First he established a relationship between the sulphur content of technical gases (Σ Sg) "gms. S/Cu. m. at N.T.P." and pS_2 whidh is the partial pressure of sulphur vapour in equilibrium with liquid iron containing sulphur, in a gaseous mixture of CO, CO_2, H_2, H_2O and N_2, and the sulphur compounds H_2S, SO_2, SO_3, CS_2, and S_2. This relationship was expressed as follows:-

$$(\Sigma Sg) = p_{S_2}^{\frac{1}{2}} \frac{1430}{P} \Bigg[\underbrace{\frac{K_2 \cdot K_3^{\frac{1}{2}}}{K_1^2} \cdot p_{H_2}}_{a} + K_3^{\frac{1}{2}} \frac{p_{CO_2}^2}{p_{CO}} \left(1 + \frac{D_{CO_2}^{\frac{1}{2}} \cdot p_{CO_2}}{D_{SO_3} \cdot p_{CO}} \right) \Bigg] + p_{S_2} \frac{2860}{P} + \underbrace{p_{S_2} \frac{2860\, p_{CO}^2}{P K_4 p_{CO_2}}}_{b} \qquad (9)$$

where:-

$$K_1 = \frac{pCO \cdot pH_2O}{p\,CO_2 \cdot pH_2} \; ; \; \log K_1 = -\frac{2203.4}{T} - 5.1588 \cdot 10^{-5}\,T - 2.5426 \cdot 10^{-7}T^2 + 7.4617 \cdot 10^{-11}T^3 + 2.3$$

$$K_2 = \frac{p^2H_2O \cdot pH_2S}{p^3H_2 \cdot pSO_2} \; ; \; \log K_2 = -\frac{11,100}{T} + 0.035 \cdot \log T + 0.0017\,T - 0.311 \cdot 10^{-6}T^2 + 2.15$$

$$K_3 = \frac{p^4CO \cdot p^2SO_2}{p^4CO_2 \cdot pS_2} \; ; \; \log K_3 = -\frac{22,636}{T} + 2.766 \cdot \log T - 0.0012\,T + 0.136 \cdot 10^{-6}T^2 + 3.488$$

$$K_4 = \frac{pS_2 \cdot p^2CO}{pCS_2 \cdot pCO_2} \; ;$$ K_4 is calculated by multiplying the equilibrium constants of the constituent reactions:- $C + S_2 = CS_2$ and $2CO = CO_2 + C$

$$D_{SO_3} = \frac{pSO \cdot p^{\frac{1}{2}}O_2}{pSO_2} \; ; \; \log D_{SO_3} = -\frac{10,373}{T} - 1.222 \cdot \log T + 13.514$$

$$D_{CO_2} = \frac{p^2CO \cdot pO_2}{p^2CO_2} \; ; \; \log D_{CO_2} = -\frac{29,500}{T} + 2.75 \cdot \log T - 1.215 \cdot 10^{-3}T + 1.35 \cdot 10^{-7}T^2 + 2.20$$

The terms marked 'a' and 'b' are very small and could be neglected. To obtain a useful graphical representation of the results, 'x' is taken as the molar fraction of CO in the CO - CO_2 mixture contained in the gases. The above expression was then given as being:-

$$P(\Sigma S_g) = p_{S_2}^{\frac{1}{2}} \cdot 1430 \cdot K_3^{\frac{1}{2}} \frac{(1-x)^2}{x^2}\left(1 + \frac{D_{CO_2}^{\frac{1}{2}}(1-x)}{D_{SO_3} \cdot x}\right) + p_{S_2} \cdot 2860 \qquad (10)$$

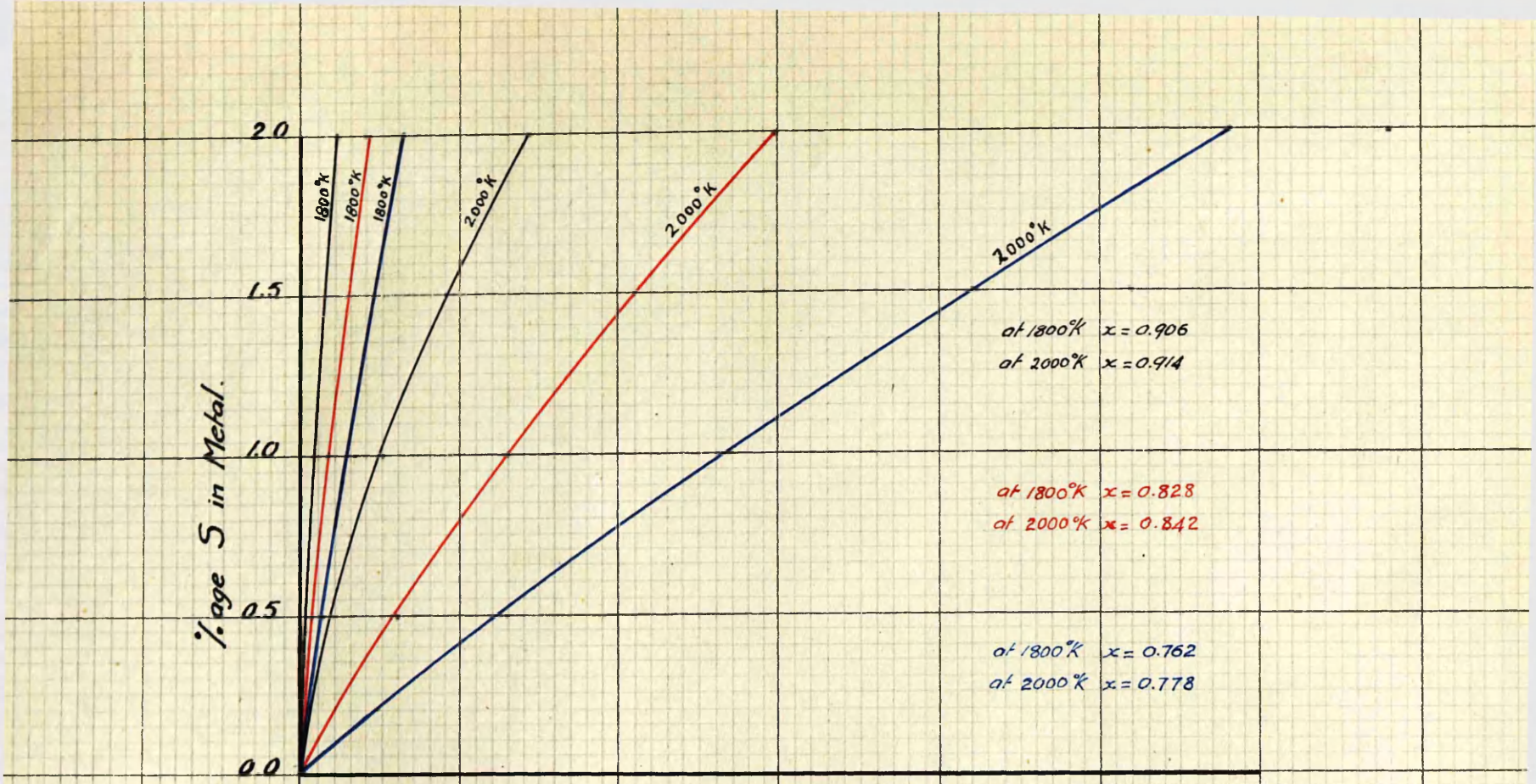


FIG 3 Sulphur content of gases in equilibrium with liquid iron at 1800°K and 2000°K.

Using equation (10) Schenck constructed a diagram giving the equilibria between the gaseous phase containing sulphur and saturated with oxygen.

In order that the effect of the state of oxidation and reduction of the atmosphere be further clarified, the author decided to construct Fig. (3) from calculations based on equation (10). Equilibrium curves are given for two temperatures, namely, 1800°K and 2000°K, and different $CO:CO_2$ ratios representing three different oxygen potentials in the system. In Fig.(3) 'x' is the partial pressure of CO in the CO/CO_2 atmosphere.

The red lines indicate the equilibrium between liquid iron containing sulphur and a sulphur-bearing gaseous phase composed of a CO/CO_2 mixture which is itself in equilibrium liquid iron saturated with FeO, the black lines indicate the equilibrium position when the CO/CO_2 mixture is in equilibrium with liquid iron containing half the saturation value of FeO, while in the case of the blue lines the CO/CO_2 ratio is such that a free FeO phase is formed corresponding to an excess of 50% over the saturation value of FeO. In all three cases the oxygen potential is the same for the two temperatures.

The oxygen content of liquid iron saturated with oxygen was calculated from the equation:

$$\log O\%_{(\text{in liq. iron})} = -\frac{6320}{T} + 2.734$$

given/

given by Taylor and Chipman[21].

The $CO:CO_2$ ratios in equilibrium with liquid iron containing oxygen, and used in the construction of Fig.(3), were calculated from the equation:

$$\log K = \frac{7320}{T} - 3.960$$

which was given by Marshall and Chipman[22] for the reaction:

$$\underset{(\text{metal})}{O} + CO = CO_2$$

Schenck's equation (10) and Fig.(3) emphasise the two most important factors affecting equilibrium between gases containing sulphur and liquid iron, i.e. temperature and the ratio $CO : CO_2$. It is clearly evident that the higher the temperature and the smaller the $CO : CO_2$ ratio the less sulphur is picked up by liquid iron from the gas.

Although this treatment is only an approximation, it is fundamentally sound and serves well to indicate the physico-chemical principles underlying the gas-metal reaction with regard to sulphur.

Schenck attributes the gas-slag reaction with regard to sulphur to the reaction:-

$$SO_2 + 3CO + CaO = CaS + 3CO_2 \qquad (3)$$

which has been given earlier by Herty. But, whereas Herty does not place any stress on the $CO:CO_2$ ratio or oxygen content of the gases but merely states that the slag is saturated/

saturated, at all times, with CO and CO_2, Schenck states that the higher the ratio pCO_2:pCO or the excess air (pO_2) in the furnace gases, the higher the ratio pSO_2:CaS(slag) will be at equilibrium, corresponding to an increased tendency for the gas to abstract sulphur from the slag. This is evident from the following equation, given by Schenck:-

$$\frac{pSO_2}{(CaS)} = \frac{K}{(CaO)}\left(\frac{pCO_2}{pCO}\right)^3 = \frac{K \cdot pO_2}{(CaO) \cdot D_{CO_2}} \qquad (11)$$

where D_{CO_2} is the dissociation constant of CO_2.

Again, equation(11) shows the importance of the ratio CO_2:CO and the activity of CaO in the slag in determining gas-slag equilibria with regard to sulphur.

Schenck states that it is inconceivable that the numerical expressions obtained by Herty[6] could hold for both oxidising and reducing conditions in the furnace atmosphere. It is equally inconceivable that the expression concerning the gas-slag reaction could hold for slags with different CaO activities.

Chipman and Ta Li[19], determined the equilibrium constant for the reaction between liquid iron and hydrogen sulphide. They obtained values one hundred times smaller than those obtained by Maurer and Bischof[17]. The result of their determination is given in the following equation:-

$$\log K = -\frac{4500}{T} - 0.343 \quad ; \quad \text{where } K = \frac{H_2S}{H_2 \cdot [FeS]} \qquad (12)$$

The/

The object of their experimental work was to determine the free energy of formation of FeS dissolved in liquid iron, i.e., for the reaction:-

$$Fe_{(liq.)} + \tfrac{1}{2}S_2 = \underset{(metal)}{FeS}$$

The free energy change is given as being:

$$\Delta G^{\circ} = -42,410 + 10.35\,T \qquad (13)$$

In dealing with the reactions between gas and bath in the open-hearth furnace, Chipman and Ta Li state that practically all the sulphur in the fuel is converted into sulphur dioxide in the furnace atmosphere and that it is unnecessary to consider either H_2S, S_2, SO_3 or SO. This view is supported by simple computations based on the free energy changes occuring during the combustion of sulphur compounds in the fuel gas.

Using equation (13), Chipman and Ta Li calculated the free energy change for reaction (6):

$$Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2 \qquad (6)$$

This is given as being:

$$\Delta G^{\circ} = 43,970 - 6.95\,T \qquad (14)$$

at 1535°C, $K = \dfrac{O_2 \cdot [FeS]}{SO_2} = 1.5 \times 10^{-4}$

If, according to Maurer and Bischof, reaction (6) represents the reaction taking place between sulphur in the furnace gases/

gases and molten iron, then, according to equation (14), no sulphur pick-up will occur above 0.00015% FeS should molten iron come in contact with a gas mixture containing equal volumes of SO_2 and O_2, any sulphur in excess being oxidised to SO_2. It is ~~is~~ quite apparent that such a state does not exist; the results obtained by Maurer and Bischof themselves providing sufficient evidence as to the soundness of Chipman and Ta Li's criticism.

Chipman and Ta Li stated that the reaction between liquid iron and sulphur dioxide is more correctly represented by:-

$$3\ Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + \underset{(metal)}{2\ FeO} \qquad (15)$$

The free energy change being:

$$\Delta G^{\circ} = -19{,}630 - 9.85\ T$$

$$@\ 1535^{\circ}C \quad K = 2.3 \times 10^{4}$$

This signifies that SO_2 in contact with molten iron would be almost entirely absorbed. That this does not take place in practice is attributed by Chipman and Ta Li to the formation of a protective oxide film which prevents direct contact between metal and gas during melting, due to the presence of excess air.

On the subject of gas-slag reactions with regard to sulphur, they gave the following reaction as being probably responsible/

responsible for sulphur removal from slag to gas:

$$\underset{(slag)}{CaS} + \tfrac{3}{2}O_2 = \underset{(slag)}{CaO} + SO_2 \qquad (16)$$

the free energy change is given as being:

$$\Delta G^{O} = -111,440 + 18.60\ T$$

$$@\ 1600^{O}C \quad K = 2 \times 10^{9}$$

Should this be the controlling reaction between gas and slag it would be practically impossible for the slag to absorb sulphur from the gas if the latter was completely combusted.

Because of the wide discrepancy observed in the results obtained by Maurer and Bischof[17] on the one hand and Chipman and Ta Li[19] on the other, in their investigation of the reaction:

$$\underset{(metal)}{FeS} + H_2 = H_2S + \underset{(liq.)}{Fe}$$

where the values obtained by the former workers for K were approximately 100 times greater than those obtained by the latter, and because of the importance of that reaction in determining the free energy of formation of FeS dissolved in liquid iron; White and Skelly[23] carried out further investigations on the above reaction and obtained values for K which were approximately one half those obtained by Chipman and Ta Li. Thus Chipman obtained:

$$\log K = -\frac{4500}{T} + 0.094$$

while/

while White obtained,

$$\log K = -\frac{4526}{T} - 0.20$$

where,

$$K = \frac{pH_2S}{pH_2 \cdot [S]}$$

In the system investigated by White and Skelly, there occured an appreciable pick-up of silicon by liquid iron, which led them to suspect that the true value of K might be lower still than that obtained by them, since it seemed probable that the silicon might increase the activity of the sulphur in liquid iron.

Recently, Morris and Williams[24], confirmed White's results and proved that silicon dissolved in iron had a pronounced effect on equilibrium conditions by increasing the activity of sulphur in iron. At a silicon content of 4%, the activity coefficient of sulphur was found to be about twice that for sulphur dissolved in pure iron.

Desulphurisation Of The Fuel Gases In The Checkers.

Although desulphurisation of fuel gases in the checkers is not directly connected with the behaviour of sulphur in the open hearth process, it has sufficient bearing on the problem to justify consideration in this work.

Dahlstrom and Ahren[12], in their investigation on the effect of sulphur in the producer gas on the sulphur content of the bath in the basic open-hearth furnace found out that an average of 35% of the sulphur in the gas is retained in the regenerator chambers, and afterwards passes off with the flue gases when the furnace is reversed. In 1932, Eisenstecken and Schulz[15], compiled comprehensive sulphur balances for open-hearth heats, taking into account the gas phase. Their results provide valuable data on the desulphurising action of the regenerators. The gas and air checkers were found to behave differently in this respect; for, while the gas checkers at temperatures of 1000°C - 1100°C retained about 60% of the sulphur in the fuel gas (a mixture of coke-oven and blast-furnace gas), the air checkers were actually introducing sulphur into the air, amounting to about 10% of the sulphur carried through the furnace with the gases.

The amount of sulphur retained in the gas checkers depended on the quantity of CaO and iron oxide deposited in the/

the checkers, the sulphur thus retained being in the form of CaS and FeS. When, however, reversal took place, the CaS and FeS in the gas checkers oxidise for the greater part and the sulphur dioxide swept out with the waste gas. At the same time the air checkers absorb sulphur from the waste gas. This meant that while sulphur was being constantly removed from the fuel gas, it was being constantly introduced into the air stream in the air regenerator. There was, however, a net reduction in the sulphur content of the gases entering the furnace amounting to about 50%.

The most recent observations concerning the desulphurisation of the fuel gas in the regenerators are given in a report "SM/A.1/46" submitted to the Steel Practice Committee by A. Robinson. The report deals with the sulphur balance for the Frodingham Melting Shop. Great difficulty in the determination of the sulphur in the waste gas was encountered due to the fact that waste gas samples taken from the gas regenerator gave a much higher sulphur content than those taken from the air regenerator. In one case the sulphur content of the waste gas from the gas regenerator was four times the sulphur content of the waste gas from the air regenerator. Another observation was the fact that the samples of waste gas taken from the gas regenerator during the first half of a reversal cycle showed a much higher sulphur/

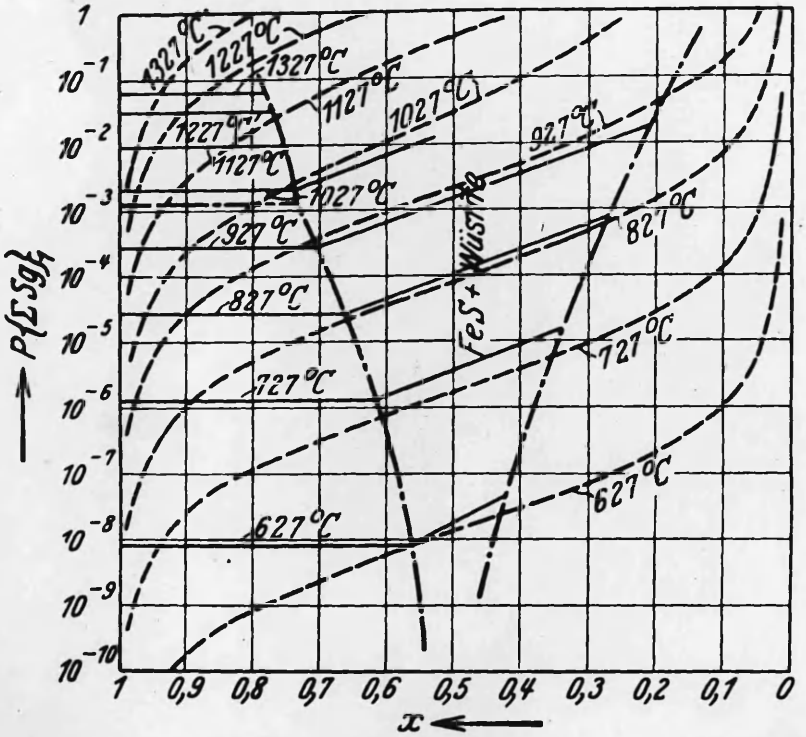


Fig. 4 —Comparison of isothermals for the equilibrium of gases containing sulphur with iron, iron oxides and iron sulphide (——), and with lime and calcium sulphide (- - - -).

sulphur content than those taken at the end of a cycle. The explanation given in the report is that absorption of sulphur from the producer gas was taking place in the gas checker and that on reversal this sulphur is evolved again as SO_2, that the gas checker was acting as a sulphur purifier, and the amount of sulphur actually getting into the furnace is considerably lower than would be expected from the sulphur in the fuel gas.

The explanation given above, together with the observations of Eisenstecken and Schulz are supported by Schenck's theoretical considerations on the possibility of the passage of sulphur from the gaseous into the solid phase and vice versa. The equilibria of gases containing sulphur with iron, iron oxides and iron sulphide, and with lime and calcium sulphide are given in Fig. (4) (taken from Schenck's work[20]), as a function of temperature and the ratio $CO:CO_2$. It is clear from the isotherms that low temperatures and reducing conditions favour the transfer of gaseous sulphur to the solid and vice versa.

It is to be concluded, therefore, that the gas regenerators, apart from their normal function, serve a very useful purpose by effectively reducing the sulphur content of the fuel gas. It should be pointed out, however, that new checkers will not act as sulphur purifiers since desulphurisation/

desulphurisation is entirely due to deposits of lime and iron oxide blown into the checkers from the furnace.

From the review of the past literature dealing with the problem of sulphur pick-up by the bath from the gas phase in the open-hearth furnace, one point of great importance seems to have gained general support, namely, that in the event of sulphur being absorbed by the bath from the furnace atmosphere, the bulk of sulphur pick-up takes place during the melting-down period. This implies that the main reaction or reactions involved are those taking place between the gas and the iron. In this respect it will not be necessary to consider any of the sulphur compounds in the furnace gases other than SO_2, since under normal conditions neither H_2S nor any other sulphur compound would be present in any significant concentration.

Two equations have been put forward to explain the reaction between sulphur dioxide and liquid iron, (6) and (15), due to Maurer and Bischof, and Chipman and TaLi respectively.

$$Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2 \qquad (6)$$

$$3Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + \underset{(metal)}{2FeO} \qquad (15)$$

These/

These reactions have been discussed above. Equilibrium calculations discredit the first reaction, while observations in practice indicate that the second reaction never proceeds to equilibrium or even to a state approaching equilibrium. To explain the failure of reaction (15) to reach equilibrium, Chipman and Ta Li state that excess air in the furnace atmosphere results in the formation of an oxide film which prevents direct contact between the liquid iron and sulphur dioxide.

It was therefore necessary as a first step in the present investigation to establish the mechanism of the reaction between sulphur dioxide and liquid iron, both in the presence and absence of free oxygen.

Platinum Resistance Furnace

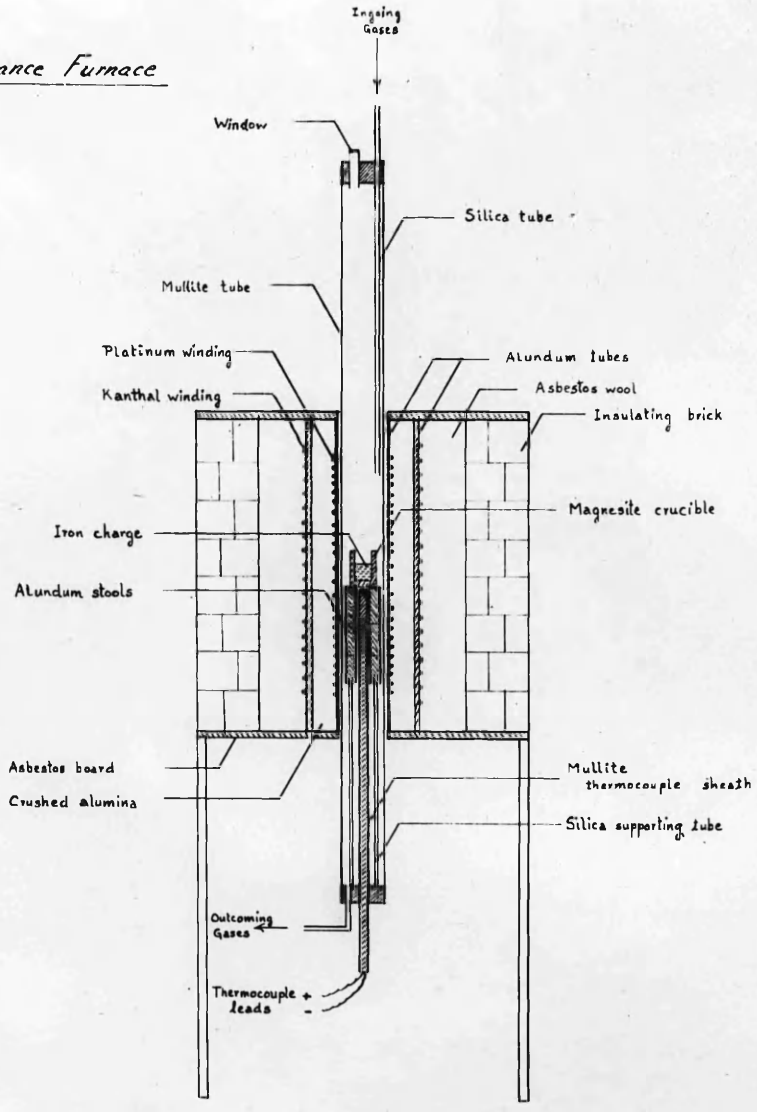


FIG. 5.

CHAPTER II.

Experimental Work On The Reaction Between Sulphur Dioxide and Liquid Iron.

The first attempt to study the reaction between SO_2 and liquid iron was carried out in a platinum resistance furnace. In this series of experiments eight runs were done of which only three were successful for reasons which will be mentioned later.

Furnace:

The furnace used is shown in Fig. (5). The inner winding consisted of 35 feet of platinum wire, 22 gauge, which was wound on an alundum tube. This was enclosed in a larger diameter alundum tube, the top and bottom thirds of which were wound with kanthal wire, 18 gauge. The space between the two tubes was filled with crushed fused alumina, 40 mesh.

The furnace was insulated with a layer of asbestos wool surrounded by an outer layer of insulating brick. This type of insulation proved to be most satisfactory. The top and bottom were made of asbestos beard ¼" thick, the whole structure being built up inside an iron frame.

The refractory furnace tubes used were Morganite triangle H5, 30" long and 1⅛" internal diameter. The outer kanthal booster coil was found to be very useful in the working of the furnace, shortening the time of heating up of the/

the furnace by half as compared with the time required when the platinum coil was used alone. The furnace attained a temperature of 1600°C @ 9 amperes, giving an even hot zone 1" long with the platinum coil alone. When the kanthal coil was kept on at 3 amperes the hot zone increased to 2".

Crucibles:

The first type of crucibles tried were made of alundum. They were fired for several hours at 1200°C in a gas muffle, but although easy to make, they proved to be quite useless as they were very badly attacked by iron sulphide and oxides which penetrated right through and attacked the furnace tube.

In a second attempt to find a suitable crucible material, fused thoria crucibles were tried, these stood up very well to the corrosive action of iron oxides but, unfortunately, apart from being expensive they were difficult to obtain at the time.

Finally, crucibles were made out of magnesite brick, kindly supplied by Messrs. J.G. Stein & Co. Ltd. These proved to be most satisfactory, and withstood the attack by iron sulphide and oxides very well. Their only disadvantage was that their manufacture was a difficult and tedious operation which also consumed a lot of time. First several holes were drilled of the required bore and depth/

depth using a high-speed steel drill which needed to be sharpened very frequently. The brick was then cut by means of a diamond wheel into rectangular blocks with the hole in the centre of each. The blocks were next ground down on a carborundum wheel to the required shape and wall thickness, dried thoroughly at 300°C and kept in a desiccator until required. Silica crucibles were never tried because it was quite obvious that they would not stand up to the action of iron oxides.

Materials Used:

1. Iron:-

Ingot Armco iron was made into bars of the required diameter. An average analysis of the iron used is as follows:

C%	Mn%	P%	S%	Si%
0.010	0.015	0.005	0.035	trace.

2. Gas:-

It was decided to use a mixture of sulphur dioxide and nitrogen first, oxygen being absent. The gas mixture was made up and stored in a 10 litre aspirator bottle. This was first filled with nitrogen which had been passed through alkaline pyrogallol to remove any oxygen which might be present. The nitrogen displaced liquid paraffin into another 10 litre aspirator bottle placed at a higher level/

level. When the bottle was filled with nitrogen the pressure inside it was brought to atmospheric pressure and a measured volume of sulphur dioxide admitted from a mercury gas burette. To insure a homogeneous gas mixture the aspirator bottle was turned from one side to the other frequently. The gas composition was checked by analysis and it was found that after 24 hours the gases were properly mixed.

Gas Analysis:

The method used for the determination of SO_2 in the gas mixture was to pass a known volume of the gasses through a known volume of 0.01N potassium permanganate solution to which a little sodium bicarbonate had been added and then to titrate the excess permanganate with standard arsenious oxide solution to determine the amount of permanganate reduced by sulphur dioxide. It was found that the liquid paraffin absorbed appreciable quantities of SO_2 at the beginning but it did not take long to become saturated after which the SO_2 content of the gas remained constant. This observation, however, made it essential to analyse the gas two or three times during any particular experiment.

Temperature Measurement:

A platinum/platinum-13% rhodium thermocouple was used which was frequently calibrated against the melting points/

points of gold and palladium. The thermocouple was placed inside a mullite sheath.

Experimental Procedure:

About 7 gms. of Armco iron were cut from the bar and placed in a magnesite crucible ½" internal diameter and ⅞" external diameter which was placed inside the furnace supported by alundum stools and a silica tube. Purified nitrogen was passed through the furnace tube and the current switched on; when the furnace attained a temperature of 1550°C the gas mixture was admitted at the rate of 150 ccs./min. The temperature and flow of gases were maintained for one hour after which the current was switched off. When sufficient cooling had taken place the crucible was removed and the iron analysed for sulphur by the conventional gravimetric method.

An attempt to follow the reaction by the analysis of the ingoing and outcoming gases, a method used by other workers who investigated gas-metal reactions[19]&[23] was not successful in this case because a considerable amount of elemental sulphur came out with the exit gases.

The crucibles were found to be impregnated with iron oxide and sulphide and presented a black appearance. The surface of the metal charge was black due to the formation of a scale. This scale was, however, very thin and adherent/

adherent and could not be separated for analysis.

Care had to be taken to keep the crucible from touching the sides of the furnace tube, otherwise, the iron oxides attack the tube and the crucible sticks to it.

Even then the tubes never survived more than three runs. An examination of the tubes after failure showed that there was a black deposit inside which had worked its way right through the material of the tubes in the region of the hot zone. This deposit was found by chemical analysis to be a mixture of FeO, Fe_2O_3 and FeS. It became quite clear that the failure of the tubes was due to the attack by iron oxides and sulphide which volatalised from the surface of the melt and deposited on the sides of the tube.

Altogether eight experiments were carried out, of which only three were successful. The others were not taken into consideration because of the failure of the furnace tube, gas supply, or the furnace itself during the run.

The above experimental set up had to be abandoned eventually because mullite tubes were unobtainable and no suitable substitute could be found.

Shortly afterwards a high frequency generator became available and it was thought that an induction furnace would be more suitable for the study of gas-metal reactions than a resistance furnace.

High/

High Frequency Furnace

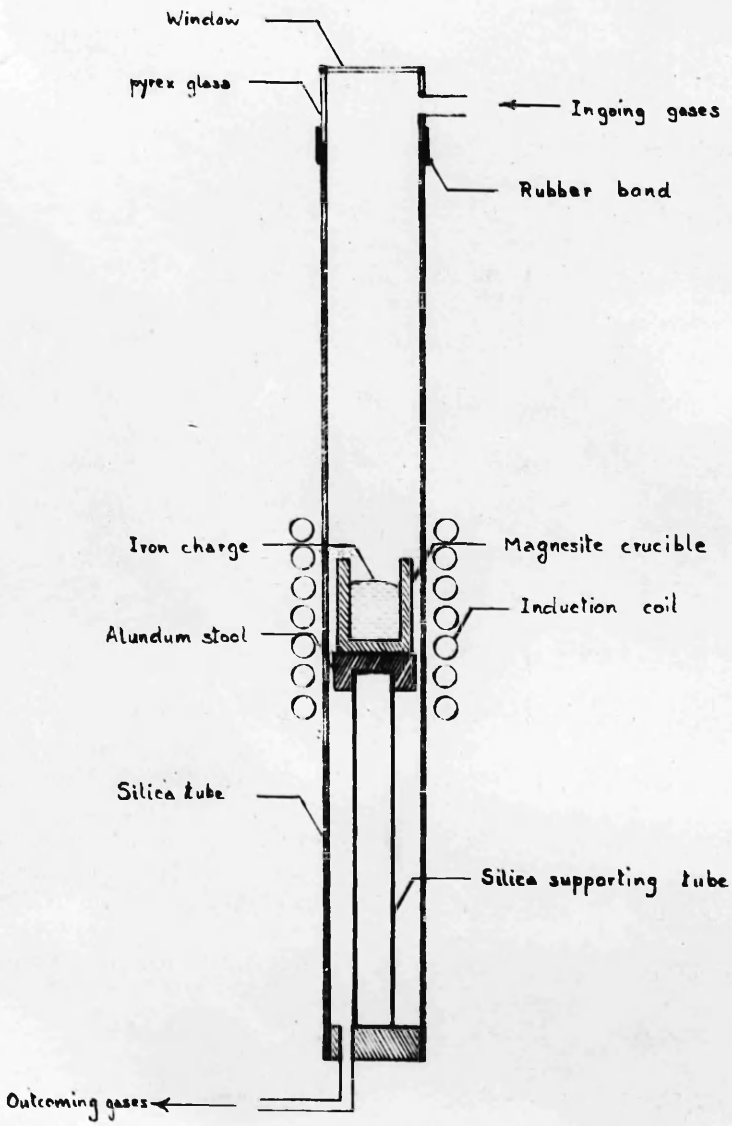


FIG. 6

High Frequency Generator:

A Philips High Frequency Generator, type F45/3 was used.

Furnace:

The first furnace used is shown in Fig. (6). It was of very simple construction, consisting of a glazed silica tube 20" long and 1½" internal diameter with a pyrex glass prolongation at the top secured by means of a piece of large bore rubber tubing. The pyrex glass extention had a glass window at the top and a side tube for the admission of the ingoing gases. The crucible rested on an alundum stool which was supported by a silica tube. The furnace tube was closed at the bottom by a rubber stopper which had an aperture for the exit gases.

The second furnace used is shown in Fig. (7). This was of a more elaborate design which allowed for the heating of the gas stream. It consisted of a glazed silica tube 12" long, 1⅝" internal diameter and 4 mm. wall thickness. This tube was fitted with water cooled brass end-sleeves with brass caps which could be screwed on and were fitted with rubber washers. The brass sleeves were cemented in place with a mixture of asbestos and water-glass and made gas-tight with a litharge-glycerine cement which was prepared by heating pulverised litharge at 400°C and then/

then mixing it with pure glycerol to the consistency of a thick paste. This dried to a very hard and impervious mass. The top brass cap was fitted with a glass window which could be screwed in place, a brass sleeve which carried a silica tube 5 mm. internal diameter to take the ingoing gases and insulated electric leads for a preheater coil. The crucible rested on an alundum stool which was supported by a silica tube. The exit gases were taken out by means of a copper tube screwed into the bottom brass cap. Water cooling was resorted to after experience with the first furnace had shown that the ends became too hot and the rubber fittings charred. An eight turn copper induction coil 2¼" diameter was used and the furnace was held in place by means of a universal stand.

Crucibles:

Now that a high frequency generator was available an attempt was made at making sintered magnesia crucibles. Burnt magnesia was used, 1/3 of which was ball-milled untill very fine and 2/3 60 mesh. The crucibles were formed dry by tamping the mixture in a graphite mould around a steel core which was then removed. The graphite mould was covered with a graphite top and fired at approximately 2000°C by induction heating for half an hour. On firing, the magnesia shrank sufficiently to allow easy removal/

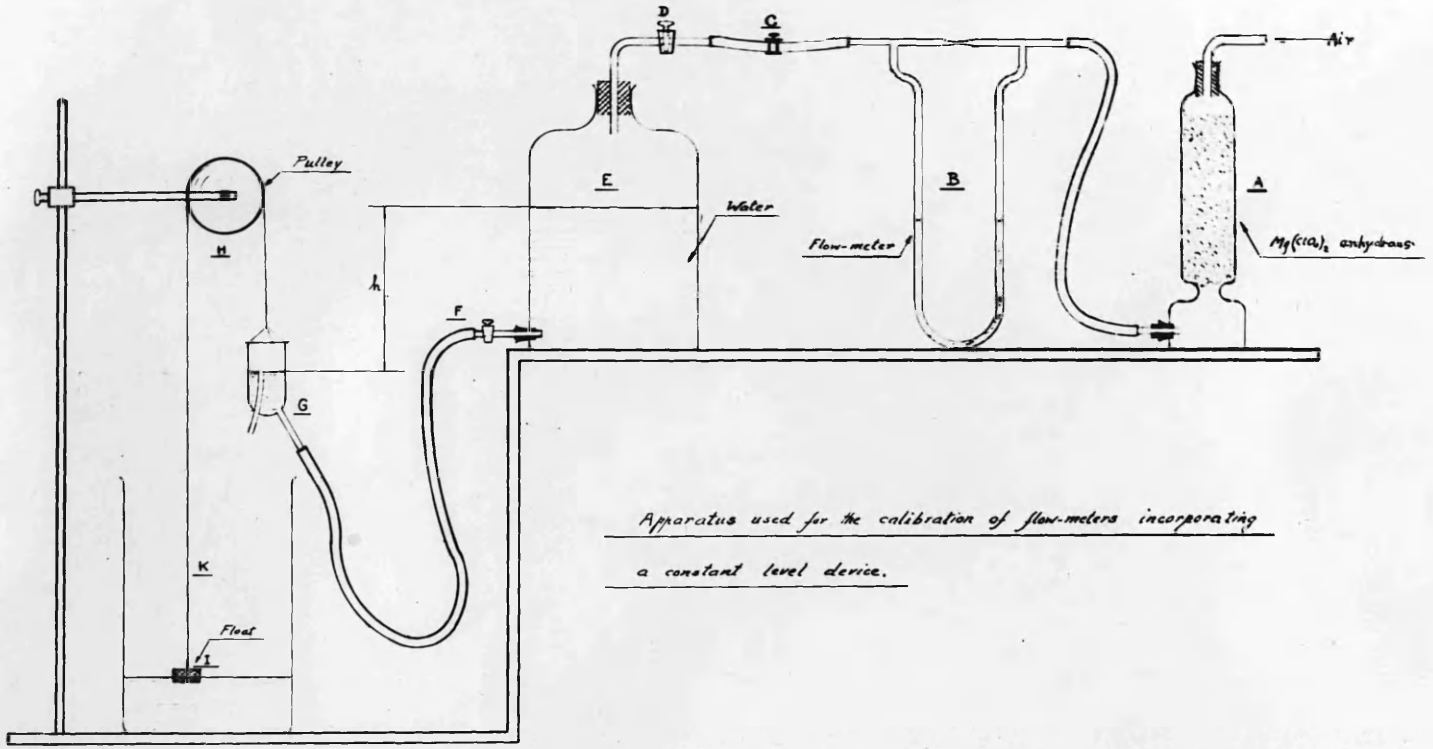
removal of the crucible, but although the crucibles were hard and had a sound appearance they invariably cracked when iron was melted in them. This was probably due to thermal stresses caused by the rapid rate of cooling which the graphite mould underwent once the current was switched off and which was unavoidable with the available set-up. It was thought that annealing at a high temperature in a Tamman furnace, followed by very slow cooling might remedy this defect, but as the purpose of the whole attempt was to save time it was thought that the old and tried method of making the crucibles out of magnesite bricks was the best.

Gas Mixture:

The method previously described for the making up and storage of the gas mixture did not prove to be quite satisfactory. On several occaisons, when there was a delay during the experiment, the supply of gas ran out, the rate of flow was inadequate and on the whole the volume was insufficient and the method of preparation lengthy and complicated.

An attempt to take the nitrogen, sulphur dioxide and oxygen directly from their respective containers was carried out with success. Ordinary cylinder nitrogen was used, it was found to contain approximately 0.2% oxygen by volume, which was removed by passing the nitrogen over

copper/



Apparatus used for the calibration of flow-meters incorporating a constant level device.

FIG. 8.

copper gauze heated to 650°C and then through three Dreschel bottles containing alkaline pyrogallol. The nitrogen was then dried by means of concentrated sulphuric acid and magnesium perchlorate. Sulphur dioxide and oxygen were taken directly from their respective containers. The rates of flow of the individual gases were determined by means of specially calibrated flowmeters.

Construction and Calibration of Flowmeters:

The flowmeters were of the usual fixed orifice type. The orifice consisted of a piece of capillary tube 1 mm. internal diameter drawn out in the middle to give a constriction. The tube was connected at both ends to a manometer which contained "Griffin and Tatlock Special Manometer Oil". Several orifices were tried until one was found to give the required range of gas flow.

A constant-level device was used to calibrate the flowmeters as shown in Fig.(8). The principle involved is to determine the volume of water displaced by the flow of dry air through the orifice per minute and noting the corresponding manometer reading. Several determinations were carried out at different manometer readings and plotted to give a calibration curve for dry air. To calibrate a flowmeter, the flowmeter in question was put in position as shown in the figure, 'E' filled with water, sufficient water was placed in 'K' to allow 'I' to float and the clip 'C'/

'C' and stop-cocks 'D' and 'F' opened. As the water level falls in 'E' and rises in 'K' the float 'I' moves upwards and 'G' moves downwards, thus keeping the distance 'h' constant since the diameters of 'E' and 'K' are identical. The rate of flow of water from 'E' to'K' and consequently the rate of flow of dry air through the orifice of the flow-meter will depend on the distance 'h'. The vertical position of 'H' is adjusted to give the required reading on 'B', then 'F' is closed and 'K' removed from its position and carefully weighed and put back in position. 'F' was opened and water allowed to run into 'K' for an accurately measured period of time, the length of which depended on the rate of flow being measured. At the same time the level in 'B' was noted. Next, 'K' was accurately weighed again, the temperature of the water taken and the volume of water, equivalent to the difference in weight, at that temperature calculated.

The calibration curves thus obtained for dry air for the different flowmeters were recalculated to give the curve for nitrogen, sulphur dioxide, etc., as the case may be. For this purpose the following formula was used:-

$$F_g = \frac{\sqrt{D_a}}{\sqrt{D_g}} \cdot F_a$$

where/

where F is flow in ccs. per minute

D is density at N.T.P.

a indicates air

and g indicates the gas in question.

Temperature Measurement:

This presented the most formidable obstacle in this work. The most obvious method of temperature measurement in this type of apparatus is by the use of an optical pyrometer. This method was found to be inaccurate under working conditions due to the fuming which took place. The size of the crucibles, mass of the charge, and the necessity for a strict control of furnace atmosphere make it impractical to take temperature measurements by the immersion thermocouple method. The following procedure was resorted to when a temperature measurement was to be taken. The charge of Armco iron was melted in an inert atmosphere and a temperature reading taken by means of an optical pyrometer of the disappearing filament type. It was noticed that about five minutes after the charge was molten the temperature reached a constant value which did not alter so long as the input voltage remained constant. Unfortunately, due to fluctuations in the mains voltage, the input voltage did not remain constant at all times and because of this several temperature measurements failed

and/

and several runs were unsuccessful due either to the solidification of the melt or to a great rise in temperature which caused the crucibles to fail.

Purified nitrogen was used to provide the inert atmosphere for temperature measurement. Although this technique was found to be quite satisfactory for the lower temperatures, above 1700°C or thereabouts fuming took place which resulted in inaccurate temperature measurements. The fumes condensed on the sides of the furnace tube in the form of a black powder, and an x-ray examination showed that it was mainly Fe_3O_4, the source of which could not be accounted for. The nitrogen did not contain any oxygen and the crucible was found to be quite clean after a run in a nitrogen atmosphere. However, hydrogen was found to be quite satisfactory for high temperature measurements. The procedure usually followed was to melt in a hydrogen atmosphere and after a constant temperature had been recorded, the hydrogen was swept out with nitrogen and the gas mixture admitted. If nitrogen was used initially, the gas mixture was just admitted as soon as the temperature was measured.

The optical pyrometer was checked against a platinum/platinum-13% rhodium thermocouple in a platinum resistance furnace up to 1600°C. Temperature readings obtained in this/

this work are considered to be accurate to within ± 10°C.

Sampling:

Segregation presented a serious problem in the sampling of the ingots produced during this work for analysis. It was found that sulphur increases both from the periphery of the ingot towards the centre and from the bottom upwards. This is in agreement with the findings of Chipman and Ta Li[19]. Examples of analyses of different parts of the ingot given in Table(1) serve to illustrate the extent of segregation taking place.

Table (1a).

Run No.	%S in sample from top crossection of ingot	%S in sample from bottom crossection of ingot	%S mean
C-9	0.4350	0.3750	0.405
C-2	1.3925	1.2375	1.315
C-15	2.5450	2.3350	2.440

Table (1b).

Run No.	%S in sample from outside of ingot	%S in sample from centre of ingot
C-15	2.426	2.705

The following method was used for sampling. First a cut was taken along the length of the ingot on the lathe to/

to remove adhering particles of crucible material, the top and bottom being cleaned in the same way. A transverse cut was then taken from both top and bottom of the ingot, both samples analysed for sulphur and the mean taken. Sound ingots were never obtained in high sulphur or in high temperature runs. These were either very porous or contained a large blow-hole. Segregation of sulphur was at its highest in the porous ingots and increased the higher the sulphur content of the ingot.

After the ingot had been sampled for sulphur it was milled, using a very sharp tool at low speed and cutting a small chip. The millings were thoroughly mixed and used for two duplicate oxygen determinations.

Analysis:

1. Determination of Sulphur:

The nitric acid gravimetric method for the determination of sulphur in iron which was used at the beginning was found to be troublesome and unsatisfactory for high sulphur contents. In these cases free sulphur appeared in the form of globules at the surface of the solution. Potassium perchlorate was added to oxidise it but this took a long time and there was always the risk of the loss of the sulphur by vapourisation.

A method which involves the solution of metallic iron in/

in acidified ammoniacal cuprous chloride solution was used with success. The following procedure was eventually evolved:

One gm. of sample in the form of fine turnings or filings was dissolved in 100ml. 30% ammoniacal cuprous chloride in 1:20 HCl. A mechanical stirrer was used. As soon as the sample was completely dissolved the solution was filtered through a Whatman No. 40 filter paper and the residue washed first with a 10% solution of the above reagent in water then with cold water. The residue was transferred to a 300 ml. beaker, 50 ml. water and 2 ml. bromine added, and heated gently. As soon as some of the bromine went into solution 5 ml. concentrated HCl were added. The heating was continued for about 30 minutes below the boiling point and then the solution was boiled to expel the bromine. The solution was filtered through a Whatman No. 41 filter paper and washed with slightly warm water. The filtrate was taken to the boil and 20 ml. of 10% BaCl solution added drop-wise with constant stirring. The precipitated $BaSO_4$ was filtered and weighed in the usual way.

The greatest source of error in this method is phosphorus, but since the Armco iron used did not contain more than 0.005% phosphorus, this source of error did not present/

Schematic diagram of apparatus used for the determination of Oxygen in iron

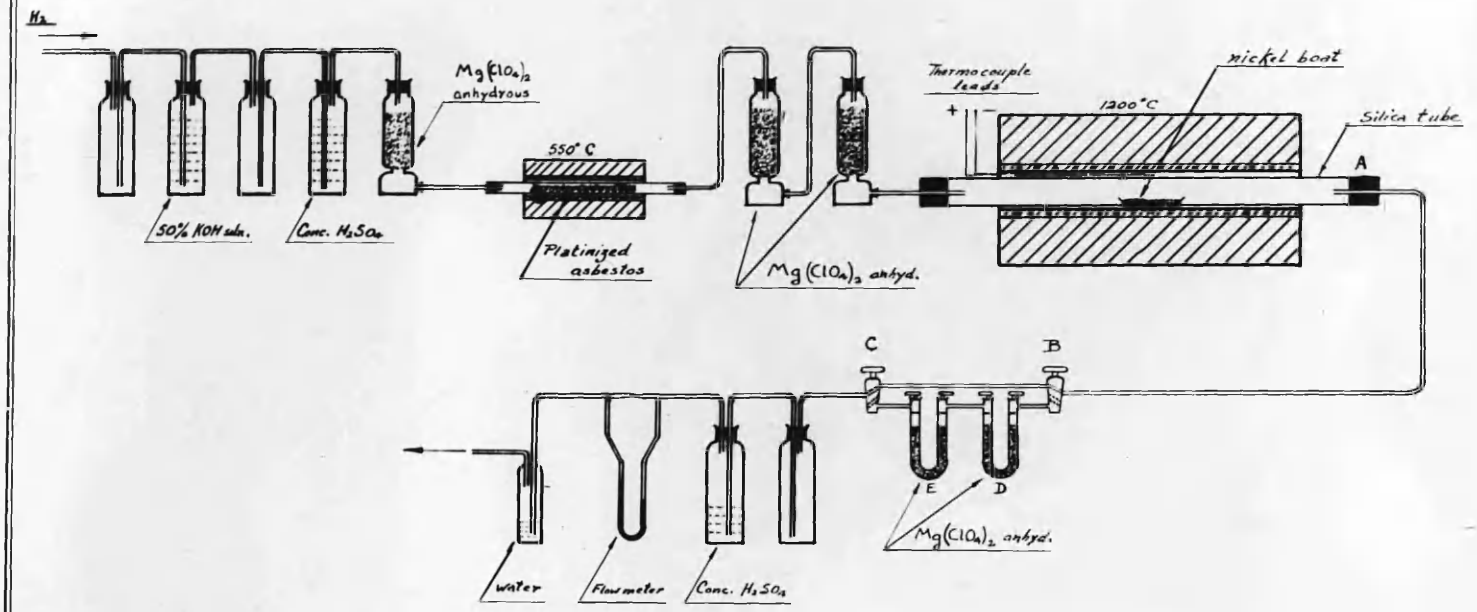


FIG. 9

present itself.

2. Determination of Oxygen:

Methods for the quantitative determination of oxygen in solid iron could be devided into:

(a) Residue methods

and (b) Reduction methods.

Residue methods depend on the solution of the metal and the analysis of the residue which will contain the oxides and inclusions. These are complicated and lengthy procedures and, furthermore, high sulphur content of the iron will cause a considerable error, since iron sulphide is not totally soluble in many of the solvents used in these methods.

The main reduction methods are two:

1. Vacuum fusion which is the most modern and generally accepted method, and,

2. Hydrogen reduction.

Apparatus for the vacuum fusion method was not available at the time of this work and consequently the hydrogen reduction method was used.

The train used is shown in Fig. (9). Compressed hydrogen was successively passed through bottles containing 50% KOH solution to remove CO_2, concentrated H_2SO_4 and a drying tower containing anhydrous magnesium perchlorate to/

to dry it It was then passed through a furnace packed with platinised asbestos maintained at 550°C. The oxygen present in the hydrogen would combine with it forming water in the catalyst furnace, the water thus formed being absorbed in two drying towers packed with anhydrous magnesium perchlorate.

The main furnace consisted of a kanthal wire coil wound round an alundum tube and insulated by means of insulating bricks. The furnace tube was made of glazed silica, 30" long and 1" internal diameter and fitted with rubber stoppers at both ends ('A' being the rubber stopper at the exit end).

A platinum/platinum-13% rhodium thermocouple was inserted between the silica tube and the furnace winding, the hot junction being at the centre of the hot zone of the furnace. After leaving through 'A' the hydrogen passed through two absorption tubes, 'D' and 'E', both fitted with stop-cocks at both ends. Two two-way stop-cocks, 'B' and 'C' could be used to divert the stream of hydrogen from the absorption tubes through a by-pass into the remaining section of the train which consisted of a concentrated sulphuric acid trap, which was also useful to provide a positive pressure in the train, a flowmeter and a small bubbler filled with water.

The/

The description given above is that of the final form of the apparatus. Originally, another furnace maintained at 260°C and containing a nickel-thoria catalyst was placed between the large furnace and the absorption tubes, its function being to convert any CO and CO_2 formed by the interaction between carbon and oxygen in the sample into methane and water vapour. The reasons leading to the disposal of the nickel-thoria catalyst furnace will be given later.

All bottles containing liquid reagents were preceded by empty ones. This precaution was necessary to prevent the reagents from mixing when an empty hydrogen cylinder was replaced by a full one. This could happen because a considerable pressure was developed in that part of the train preceding the reduction furnace.

An essential condition in this apparatus is that it should be free from leaks and a minimum of rubber tubing used since rubber tubing tends to retain moisture very tenaciously. During trial runs the 'blank' value was found to be quite considerable; furthermore, the value was not constant. An analysis of the hydrogen used, kindly provided by the British Oxygen Company, is given in Table(2).

Table/

Table(2).

CO vol./1,000,000	8.4 - 16.0
CO_2 vol./1,000,000	3 - 22
Other carbon compounds as CO_2 vol./1,000,000	19 - 58
O_2% by volume	0.005 - 0.2
N_2% by volume	0.04 - 0.75
NH_3 vol./1,000,000	0.16 - 4.5
Hg as vapour gms/10^5 per ft^3	1
SO_2 and SO_3	Beleived absent

It became evident that the nickel-thoria catalyst furnace might be responsible for the high 'blank' obtained as it would be converting the CO and any CO_2 not absorbed by the KOH into methane and water. There were two alternatives in dealing with this situation, either to introduce another nickel-thoria catalyst furnace at the beginning of the train to remove CO and CO_2 or to remove the nickel-thoria furnace altogether. The latter alternative was adopted, since the carbon content of the samples was exceedingly low, to the extent that any error caused by its combining with the oxygen in the iron would be negligible. Subsequent trials showed that although the blank value did not show a great drop, it became very constant and reproducible. A possible explanation for the persistence/

persistence of the blank will be given later.

After several trials the following technique was developed. A nickel boat, 10 cms. long, 15 mms. wide and 10 mms. deep was inserted into the centre of the silica tube and the rubber bung 'A' secured in place. The apparatus was tested for leaks by evacuation. The hydrogen was then made to flow at the rate of 1000 ccs./min., a fine-adjustment valve being necessary to maintain an accurately controlled rate of flow. The furnaces were then switched on, the catalyst furnace being maintained at 550°C and the large furnace at 1200°C. Stop-cocks 'B' and 'C' were adjusted so as to divert the gas stream from absorption tubes 'D' and 'E' and allowing it to pass directly to the atmosphere through the sulphuric acid trap and flowmeter, the hydrogen being ignited after its exit from the bubbler. These conditions were maintained for a whole day (about 10 hours) after which the gas flow was reduced to about 10 ccs./min., the temperature of the large furnace lowered to 600°C and the apparatus left in this condition overnight. This procedure insured the complete dryness of the apparatus.

A 'blank' determination was carried out before each oxygen determination by the following method: The gas flow was increased to 1000 ccs./minute and the large furnace/

furnace maintained at 600°C for exactly one hour. The stop-cocks 'B' and 'C' were then turned so as to allow the hydrogen to pass through the absorption tubes for five minutes, at the end of which time absorption tube 'D' was removed, accurately weighed, and put back in its place. The temperature of the large furnace was then increased gradually and regularly to 1200°C during one hour and kept at that temperature for another hour. Next, 'D' was removed and weighed again. This gave the 'blank' value, which varied from 0.0025 gms. to 0.0030 gms. throughout the series of oxygen determinations. This is rather a high value but so long as the rate of flow of hydrogen, temperature and time factors were kept strictly constant the blank value remained reproducible to within a limit of 0.0003 gms.

The only possible explanation for the high 'blank' value obtained is that the silica of the furnace tube is reduced to a slight extent by the action of hydrogen at high temperatures. This explanation finds support in the fact that when the furnace temperature is kept at 600°C the blank value falls to about 0.0008 gms.

To carry out a determination, the temperature of the large furnace was brought down to 600°C (to save time the top half of the furnace was removed). The stopper 'A' was removed and simultaneously the hydrogen was ignited, the/

the nickel boat withdrawn and stopper 'A' replaced. An accurately weighed sample of millings weighing about 7 gms. was placed in the boat which was returned to the hot zone of the furnace in the same way it was removed. The procedure adopted in carrying out a blank determination was then repeated in every detail.

Throughout the series of oxygen determinations, hydrogen was allowed to flow through the apparatus and the furnace kept running. The fact that the silica tube was constantly kept at 600°C when not in use prevented devitrification from setting in although it was being heated at 1200°C for a considerable period of time. It was noticed, however, that the glaze on the interior of the middle of the tube wore off, no doubt due to the action of hydrogen on the silica at high temperatures.

It can be seen from the description given above of the procedure followed that about seven hours were required to carry out one blank and one oxygen determination. It therefore follows that only one oxygen determination was possible per day. All oxygen determinations were carried out in duplicate and the mean taken after subtracting the value of the blank determination from each.

It should be emphasised that the strictest control of the rate of flow of hydrogen, temperature and time should be/

be observed and is most essential if the results are to be reproducible.

Although the method might be inherently inaccurate for the determination of oxygen combined in iron as FeO or dissolved in the iron, it was shown experimentally to give reproducible results and, therefore, could be relied upon to provide a good and accurate comparison of the oxygen contents of the samples.

Experimental Procedure:

A magnesite crucible containing 15-20 gms of Armco iron was placed in the high frequency furnace and the top and bottom secured firmly in place. The gas mixture was then admitted at the top and led from the bottom into a small bubbler containing H_2O_2 to absorb the sulphur dioxide. After the gases had been allowed to flow through the furnace for 15 minutes at the rate of 350 ccs./minute, the current was switched on. Melting was complete in about five minutes and the furnace was kept running for a period of time at the end of which the current was switched off. Solidification started after about 10 seconds and was complete in another 10 or 15 seconds. When sufficient cooling had taken place the crucible was removed and broken, and the ingot cleaned, sampled and analysed for sulphur and oxygen as mentioned before. Throughout the run the/

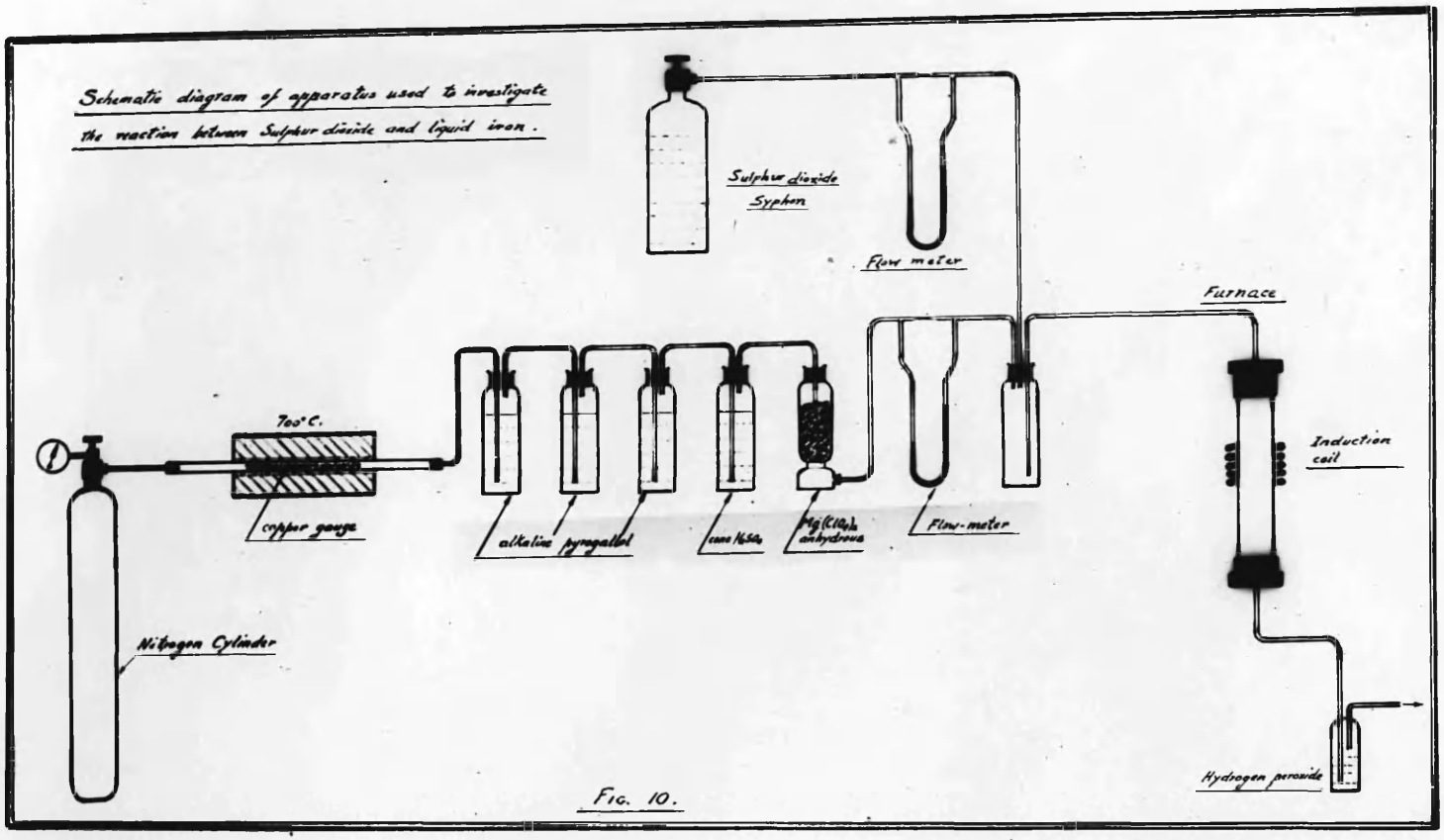

Schematic diagram of apparatus used to investigate the reaction between Sulphur dioxide and liquid iron.
Sulphur dioxide
Syphon
Flow meter
Furnace
Induction coil
700° C.
copper gauze
alkaline pyrogallol
conc H2SO4
Mg(ClO4)2 anhydrone
Flow-meter
Nitrogen Cylinder
Hydrogen peroxide

FIG. 10.

the flowmeters were watched to ascertain that the gas composition did not alter.

The procedure followed when taking a temperature measurement has been described earlier. A schematic diagram and photographs of the apparatus used are given in Figs.(10),(11a),and(11b).

Results and Observations:

I. Experiments With Gas Mixtures Consisting Of Sulphur Dioxide And Nirogen:

Over 60 runs were carried out, of which 45 were successful. All the results are given in Table(3) and shown graphically in Fig.(12).

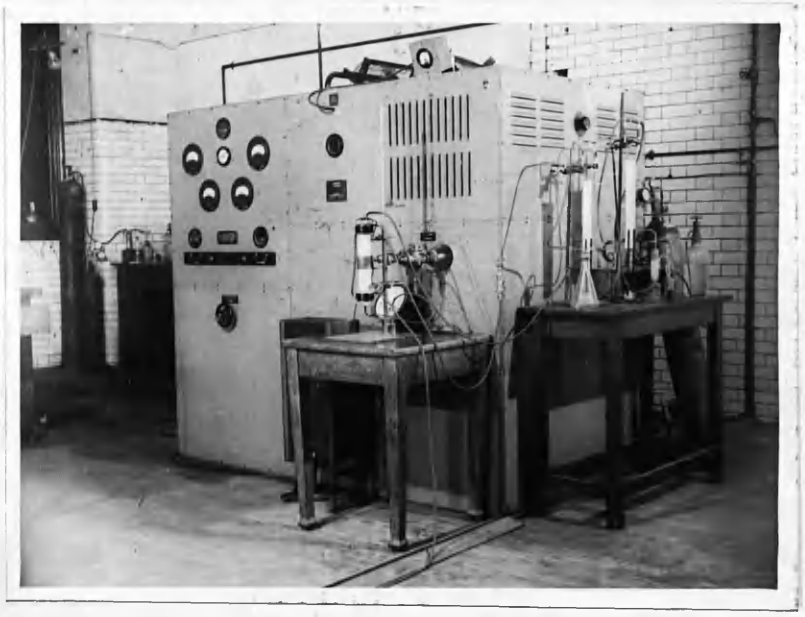


Fig 11a- View of apparatus used for the investigation of the reaction between sulphur dioxide and liquid iron.

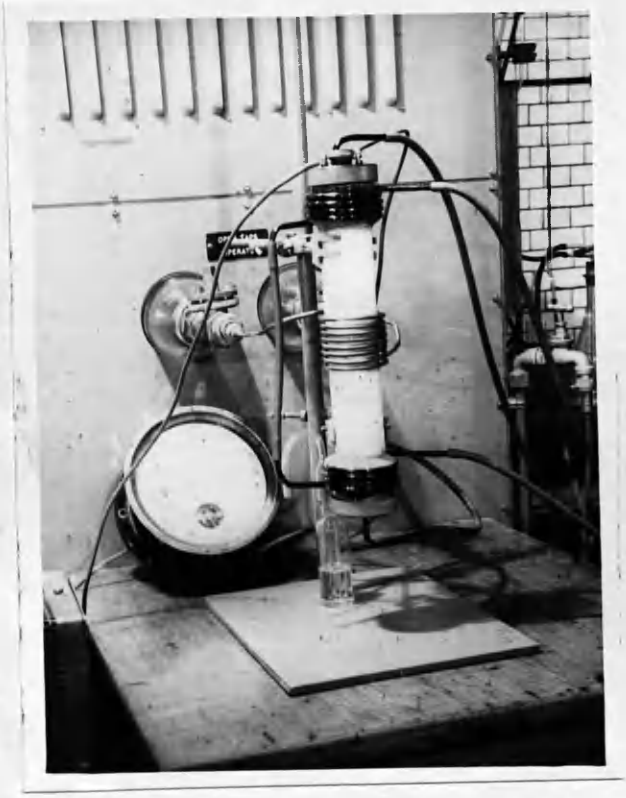


Fig 11b- View of high frequency furnace, showing watercooling arrangement and gas preheater connections.

TABLE (3).

Run No.	pSO_2 atmos.	%S in metal	%O in metal	Time minutes	Temp. °C.	Remarks
A-3	0.00880	0.295		60	1550	
4	0.00845	0.300		"	1550	Carried out in platinum furnace. Temperature measured by platinum/ platinum - 13% rhodium thermocouple.
6	0.00840	0.355		"	1550	
C-1	0.0265	0.0460		10		
2	0.0452	1.015		"		
3	0.0640	1.740		"		
4	0.0149	0.505		30		
5	0.0187	0.850		"	1600	
6	0.0425	1.70		"		Carried out in high frequency furnace. Gas not preheated. Metal completely inside crucible. Temperature measured by optical pyrometer. Believed to be accurate to within ± 10°C.
9	0.0145	0.405		60		
10	0.0382	1.35	0.346	"	1750	
12	0.0675	2.94	0.208	"	1650	
13	0.0125	0.54		30		
15	0.0556	2.44		"	1640	
16	0.0640	2.74	0.211	"	1650	
D-1	0.0660	0.22		"		

TABLE (3) contd.

Run No.	pSO_2 atmos.	%S in metal	%O in metal	Time minutes	Temp. °C.	Remarks
D-2	0.0153	0.46		30		As in C - but metal projecting from crucible.
3	0.0583	2.20		"	1760	
E-1	0.0081	0.18		"		
2	0.0149	0.23		"	1850	
3	0.0529	2.31		"	1610	
4	0.0084	0.175		60		
5	0.0258	0.81		"		
8	0.0314	1.075		"		As in C - but gas preheated. Preheater coil at 1200°C approx.
10	0.0125	0.46		75		
14	0.0161	0.42		"		
15	0.0525	1.982	0.333	"	1750	
16	0.0155	0.45		30		
17	0.0133	0.65		"	1650	
18	0.0190	0.45		"		
19	0.0142	0.325	0.378	60	1750	

TABLE (3) contd.

Run No.	pSO_2 atmos.	%S in metal	%O in metal	Time minutes	Temp. °C.		Remarks
G-1	0.0170	0.53		30			
2	0.0174	0.475		"			
3	0.0271	1.32		"	1530		
4	0.0417	1.73	0.236	"	1650	As in E.	About 0.5 gms. Fe_2O_3 added to melt.
7	0.0455	1.92	0.230	"	1650		
8	0.0523	2.01		"			
H-1	0.0076	0.23	0.261	"	1650		
2	0.0144	0.51	0.275	"	1650		
3	0.0455	1.865		"			
4	0.0203	0.55	0.374	"	1750	As in C.	
5	0.0238	0.71	0.372	"	1750		
7	0.0619	2.32	0.325	"	1750		
K-1	0.0080	1.28		45	1700	As in C.	Started with iron containing 1.38% sulphur.
2	0.0070	1.16		40	1780		

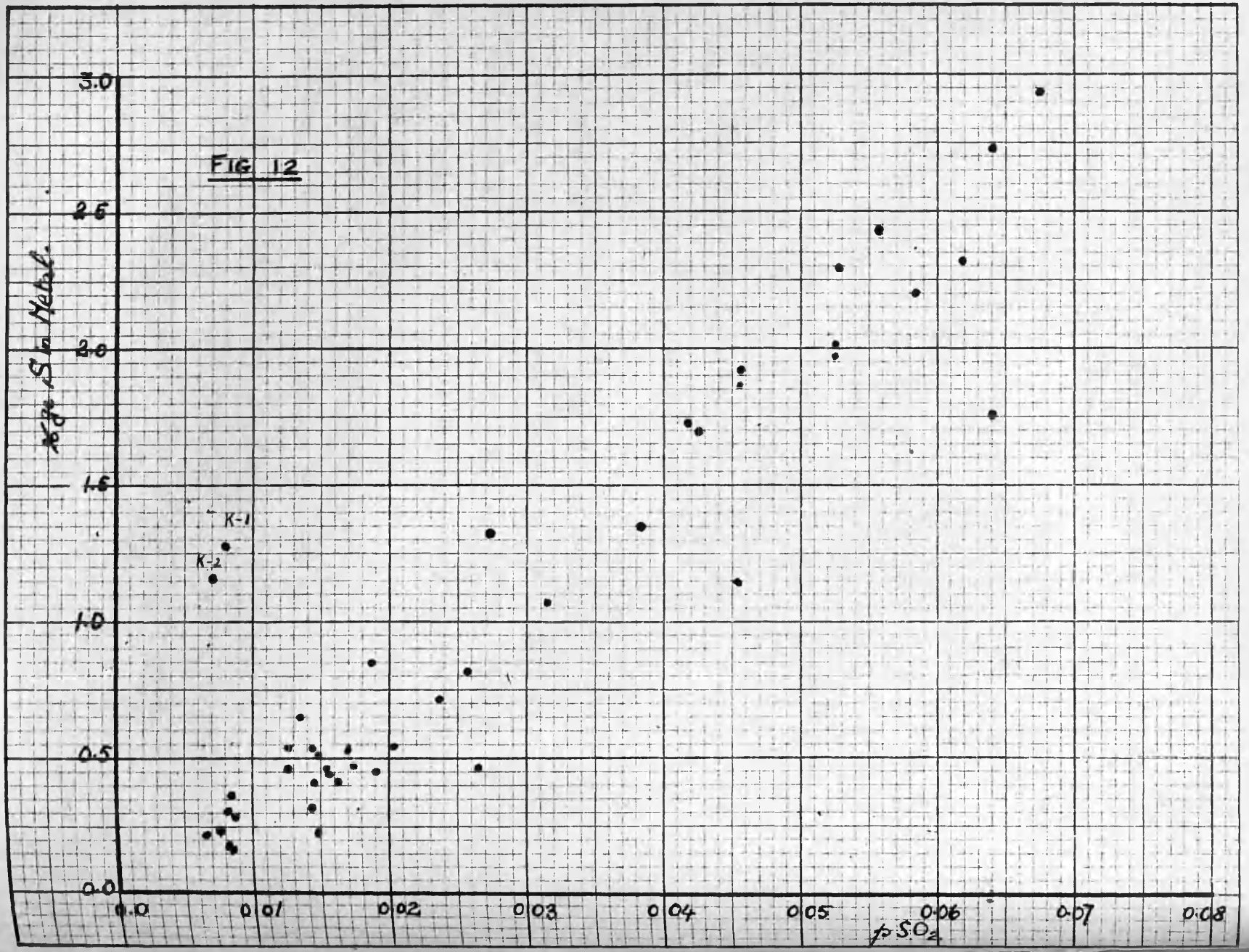


FIG 12
3.0
2.5
2.0
1.5
1.0
0.5
0.0
K-1
K-2
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
$p SO_2$

The first series of experiments carried out in the induction furnace still gave sulphur contents far less than that expected from equation (15) and not very different from those obtained in the resistance furnace. Because of this all possible sources of error were investigated.

1. It was ascertained that no oxygen was coming into the system either with the nitrogen or through leakage.

2. The time of attainment of equilibrium was investigated. A series of runs was carried out using the same weight of iron and the same rate of flow of gases but different periods of time for the runs, namely, 10 minutes, 30 minutes, 60 minutes and 75 minutes. It was found that for a charge of 15 gms and a rate of flow of 350 ccs/minute 10 minutes were not sufficient but that a period of over 30 minutes did not alter the sulphur content of the metal. The effect of time of reaction is shown in Fig. (13).

3. It was suggested that a 'dead space' might form in the crucible over the liquid iron, therefore, a series of runs was carried out in shallow crucibles so that the liquid metal actually projected out of the crucible in the form of a convex surface. The metal thus came into good contact with the furnace atmosphere and, therefore, eliminated the possibility of the formation of a 'dead space' over the/

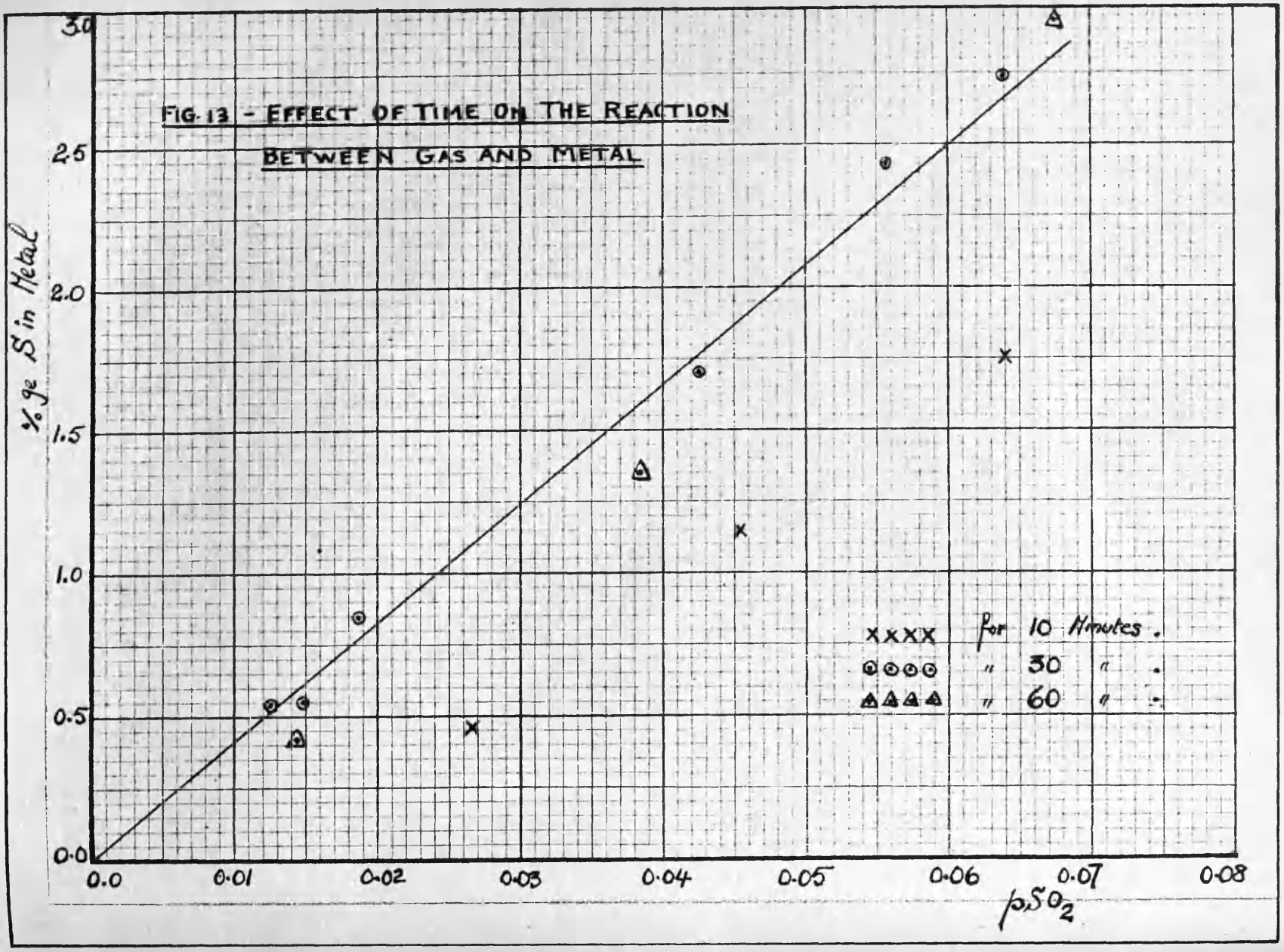


FIG. 13 - EFFECT OF TIME ON THE REACTION BETWEEN GAS AND METAL
% ge S in Metal
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
p_{SO_2}
XXXX For 10 Minutes.
⊙⊙⊙⊙ " 30 " "
△△△△ " 60 " "

the melt. This did not alter the results either.

4. It was quite possible that the wide discrepancy observed between the results obtained and those theoretically expected was due to thermal diffusion taking place in the system. This possibility could only be investigated by preheating the gas stream before it came in contact with the liquid iron. The furnace used hitherto had been of very simple construction, with no provision for preheating the gases. In order to do this, another more elaborate furnace was constructed and which was described earlier. The preheater consisted of a silica tube 5 mms internal diameter and about 5" long. A coil of nichrome wire 24" gauge and five feet long was inserted into the silica tube. The ends of the coil were led out through two holes bored in the tube and were attached to the insulated leads in the brass top. The two holes were blocked with a little alundum cement. The coil was heated at about 1200°C which is the maximum temperature for both nichrome and silica, the gases were assumed to reach a temperature of about 1000°C. The end of the preheater projected inside the crucible. Although there was no evidence of attack on the nichrome by SO_2, the coils rarely survived more than two runs as their lower end always fused due to the radiant heat from the surface of the melt.

Several/

Several runs were carried out with the preheater on, the runs lasting for different durations. The surprising thing was that it had no noticeable effect on the amount of sulphur taken up by the melt from the gases as shown in Fig. (14). It is recognised that for an efficient preheat, the gases should be brought to the temperature of the melt or as near to it as possible. Unfortunately, no better preheat was possible because refractory tubes of suitable dimensions and capable of withstanding higher temperatures were unobtainable at the time. Nevertheless, if thermal diffusion did introduce a big error in the system under consideration then even the inefficient preheat which was applied to the gases should have produced a noticeable difference in results.

It is to be concluded, therefore, that thermal diffusion does not take place to the extent of introducing a noticeable error in the system under consideration.

In order to confirm these conclusions on the probable effect of thermal diffusion, the problem of the latter will be examined in greater detail in a later chapter.

5. As all previous attempts to approach equilibrium between sulphur dioxide and liquid iron have been carried out from the low sulphur side, there naturally existed the possibility that the reaction did not, in fact, reach equilibrium/

equilibrium but merely came to a standstill for some reason or other. Although it was found that no additional sulphur was taken up by the melt from the gases once a certain period of time had elapsed, it was quite possible that the rate of reaction slowed down to such an extent that a much longer time would be necessary to show an increase in sulphur content. To settle this question it was decided to approach equilibrium from the high sulphur side. A high sulphur alloy was prepared by adding FeS to molten Armco iron in a known proportion. After the melt was thoroughly mixed it was cast in a cold steel mould, solidification being very rapid. The FeS was prepared by mixing electrolytic iron powder with flowers of sulphur in stoichiometric proportions and igniting the mixture in a nitrogen atmosphere. Two pieces, 20 gms each, were sawn off from the rod and each was sampled for analysis. The sulphur content was found to be 1.388% for both. These two high sulphur samples were then melted in the high frequency furnace in a SO_2- N_2 atmosphere in exactly the same way as described earlier. The sulphur dioxide concentration in the gas mixture was kept slightly below 1.0% by volume. The duration of both runs was 45 minutes at two different temperatures. The resulting ingots were sampled and analysed for sulphur in the usual way. The results/

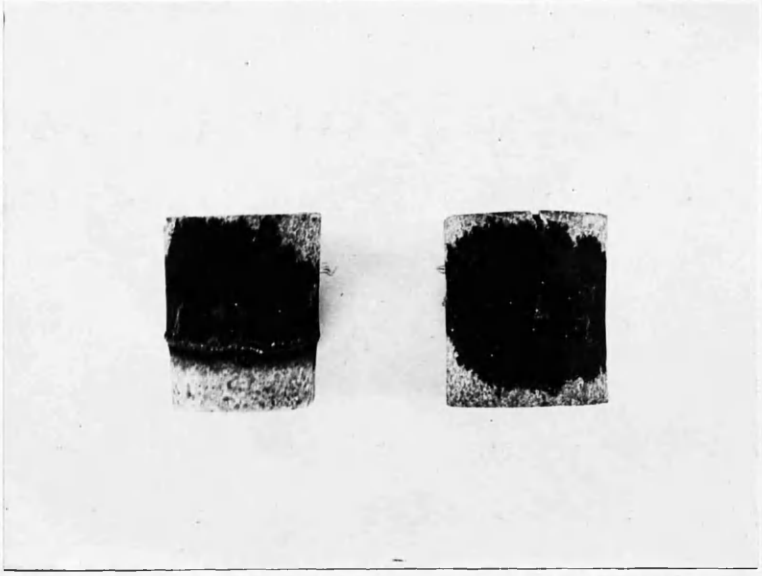


Fig 15- Two magnesite crucibles after a run lasting for one hour, showing cracks and impregnation of crucible walls with FeO-FeS slag.

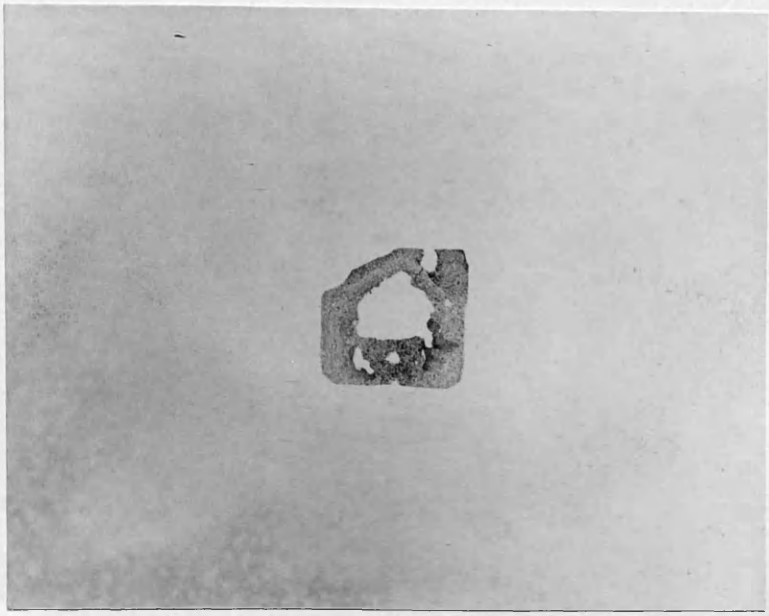


Fig 16- Sulphur print of vertical section in ingot obtained from run D-3.

results are shown in Table(3), series'K' and in Fig.(12).

From the analysis it is clear that the sulphur content has fallen, it is also obvious that the rate of sulphur removal is much slower than that for its absorption by liquid iron.

All the crucibles, after a run of 30 minutes, were impregnated right through in places with iron oxides and sulphide in the form of black patches. The longer the duration of the run the larger the patches. Moreover, most of the crucibles developed cracks at the beginning of the run; these cracks, however, did not actually lead to the failure of the crucibles during a run lasting for 30 to 45 minutes but frequently did so during runs lasting for 60 minutes or more. Fig.(15) shows two crucibles after a run lasting for one hour, the penetration of the iron oxides and sulphide and the cracks being well illustrated.

In all the experimental runs carried out fuming took place from the surface of the melt. At low temperatures it was slight and did not interfere to a great extent with temperature readings. These, however, were never taken as being reliable. At high temperatures, however, fuming was very intense. The fumes condensed on the sides of the furnace tube in the form of a black deposit/

deposit in the upper end and a brown deposit in the centre; that is, in the hot region of the furnace. In not one instance did a visible and removable layer of slag form on top of the melt. In an attempt to produce such a layer of slag series 'G' was carried out, in which about 0.5 gms Fe_2O_3 were placed together with the iron charge but this attempt was not successful as all the oxide was absorbed by the crucible. Attempts to obtain a slag by adding about 2 gms of Fe_2O_3 to the iron charge were unsuccessful due to the failure of the crucibles under such conditions.

Table(4) shows the results of analyses conducted on the black deposit from the interior of the furnace tube. The brown deposit formed in the centre of the furnace tube could not be isolated for separate analysis.

Table(4).

Run No.	%FeS	%FeO
E-1 to 5	3.02	96.98
E-15 to 19	2.86	97.14

The process of solidification of the ingots, which was observed in all cases, is of interest. Solidification started from the periphery of the crucible about 5 to 10 seconds after the current was switched off. After a rim

Fig 17a- Ingot obtained from run D-2. Sulphur content 0.46%.

Fig 17b- Ingot obtained from run D-3. Sulphur content 2.20%.

was formed gas evolution took place in all cases. It is worthy of note that the amount and rate of gas evolution depended entirely on the temperature, in high temperature runs gas evolution was considerable. This continued for 10 - 15 seconds after which the core of the ingot solidified. The last gas bubbles usually raised the top of the ingot into the shape of a dome, Fig. (17). This protrusion which appears during the final stage of solidification contains a higher percentage of sulphur than any other part of the ingot. All ingots contained a comparatively large blow-hole and most were also porous, the internal structure of the ingots being shown in Fig. (16).

The gas evolved during solidification could only be sulphur dioxide, since no such gas evolution took place during the solidification of iron which had been kept in the molten state for at least 30 minutes in an atmosphere of pure nitrogen; such ingots contained a very small pipe and were non-porous.

Another observation which was of interest was the fact that once the iron charge was molten, elemental sulphur came out with the exit gases. This persisted throughout the sries of experiments. After some time, sulphur was also found to be deposited on the cold lower end/

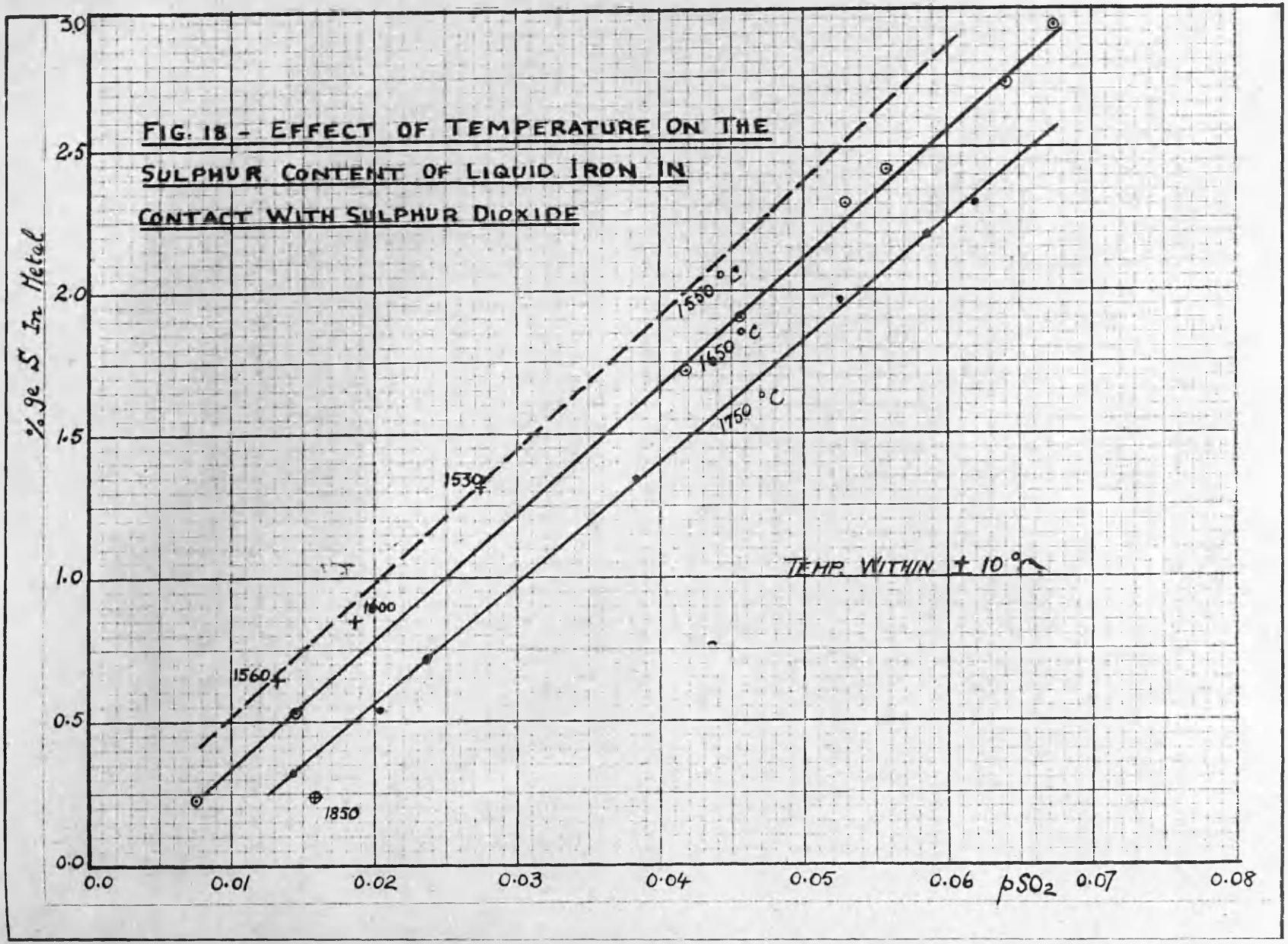


FIG. 18 - EFFECT OF TEMPERATURE ON THE SULPHUR CONTENT OF LIQUID IRON IN CONTACT WITH SULPHUR DIOXIDE
% Se S In Metal
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
pSO2
1550 °C
1650 °C
1750 °C
1530
1600
1560
1850
TEMP. WITHIN ± 10 °C

end of the furnace tube. This phenomenon was dependent on the temperature and the sulphur dioxide concentration in the gas mixture, increasing considerably with increase of both factors.

The effect of temperature is quite pronounced, low temperatures being more favourable to the pick-up of sulphur by liquid iron from sulphur dioxide. This is shown in Fig. (18).

II. Experiments with gas mixtures consisting of sulphur dioxide, nitrogen and oxygen:

In investigating the reaction between liquid iron and sulphur dioxide in the presence of oxygen the same apparatus and procedure were used as described earlier, with the addition of a third flowmeter to measure the flow of oxygen into the gas mixture.

Eleven runs were carried out of which eight were successful. In series 'L' the sulphur dioxide content of the gases was kept fairly constant while the oxygen content was varied. In series 'M', on the other hand, it was the oxygen content which was held constant.

Ten minutes after the commencement of the run a slag layer became visible, appearing in the form of a rim round the liquid iron due to the convexity of the surface of/

of the melt which is characteristic of high-frquency melting. The slag rim increased in area as time went by.

Temperature measurement was carried out as described earlier; it was evident, however, that if an excessive volume of slag was allowed to form, covering a large area of liquid iron, the initial temperature would be altered since the slag would tend to decrease heat radiation from the surface of the liquid iron and the temperature would consequently rise. For this reason the oxygen content of the gas mixture was restricted to the range 1% to 6% by volume. This range, while adequate to indicate the effect of oxygen on the reaction between sulphur dioxide and liquid iron, would provide sufficient slag for analysis without throwing the temperature of the melt off the measured value at the commencement of the run. It has been mentioned earlier that temperature measurements during or at the end of the run are not regarded as reliable due to the fuming which takes place from the surface of the melt.

The weight of the charge did not exceed 15 gms., and the duration of each run was 45 minutes. A flow of about 350 ccs/min. was maintained.

In all the runs liquid iron was constantly in direct contact/

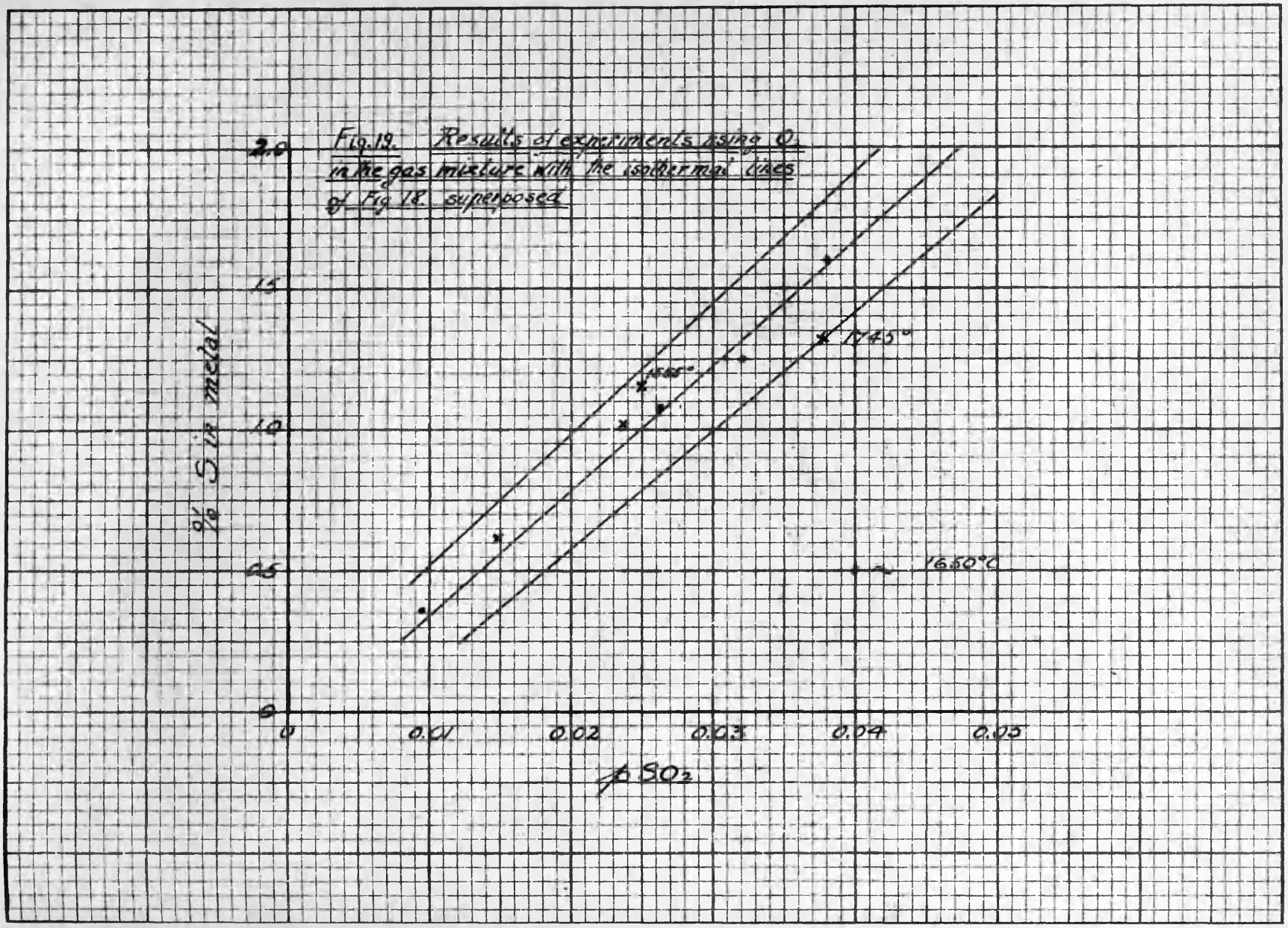


Fig. 19. Results of experiments using O_2 in the gas mixture with the isothermal lines of Fig. 18. superposed
2.0
1.5
1.0
0.5
0
% S in metal
0
0.01
0.02
0.03
0.04
0.05
% SO_2
1545°
1645°
1650°C

contact with the gases and in no instance did the slag intervene completely between them.

An interesting point is that no elemental sulphur was observed to result from the reaction between liquid iron and sulphur dioxide in the gas mixture. Fuming was observed to take place throughout the runs, the deposit which formed inside the furnace tube being still abundant but of a different colour, being reddish brown instead of greyish black as was the case when no oxygen was introduced into the gas phase.

The appearance of the crucibles and the internal structure of the ingots remained unchanged.

The ingots were sampled and analysed for sulphur as described earlier, the slag rim was analysed for sulphur and total iron, the results of the slag analyses being given in terms of FeO and FeS per cent.

The results are given in Table(5). Fig.(19) shows the relationship between the sulphur content of the metal and the partial pressure of sulphur dioxide in the gas mixture.

Table/

Table(5).

Run No.	pSO_2	pO_2	%S in metal	Temp. °C.	Time.	%FeO (slag)	%FeS (slag)	$\frac{pSO_2}{pO_2}$
L-2	0.0250	0.0166	1.153	1555	45'	94.32	5.68	1.51
3	0.0263	0.0219	1.083	1650	45'	95.46	4.54	1.20
4	0.0378	0.0425	1.317	1745	45'	95.12	4.88	0.89
7	0.0237	0.0606	1.021	n.d.	45'	95.37	4.61	0.39
M-1	0.00966	0.0408	0.358	1645	45'	98.38	1.62	0.237
2	0.01484	0.0404	0.610	n.d.	45'	97.63	2.37	0.367
3	0.03208	0.0415	1.248	1645	45'	94.49	5.51	0.774
4	0.03800	0.0410	1.603	1650	45'	93.20	6.80	0.927

CHAPTER III.

Thermal Diffusion.

Chapman[25], in 1917, in his analysis of molecular motions, obtained an equation of diffusion which indicated that the causes of diffusion are: 1- A concentration gradient or variation in the relative properties of the two component gases. 2- External forces of unequal amounts per unit mass of the two gases. 3- Variation in the total pressure or the temperature of the composite gases.

The discovery that diffusion could be caused by a variation in the temperature of the composite gases was made possible by the fact that in his theoretical treatment Chapman assumed that the gas molecules behave like rigid elastic spheres. Hitherto, an accurate mathematical treatment could only be conducted on Maxwellian molecules, which are point centres of force varying inversely as the fifth power of the mutual distance 'r', in which case thermal diffusion will not take place. Pursuing the theoretical treatment of this phenomenon, Chapman showed that thermal diffusion could only take place if the masses or diameters of the molecules are not the same for the two gases, and that the heavier gas will tend to diffuse towards regions of lower temperature and vice versa for the lighter gas. He denoted

the/

the coefficient of ordinary diffusion in gases D_{12} and that for thermal diffusion D_t. So, if a temperature gradient were imposed upon a uniform mixture of two gases, in the absence of any other agent which tends to produce diffusion, the heavier gas molecules will diffuse in the direction of diminishing temperature and vice versa for the lighter gas molecules; there will be a limit, however, to the inequality of composition thus set up, since such an inequality will tend to correct itself by the process of ordinary diffusion. When a system reaches equilibrium with regard to thermal diffusion the amount of resulting concentration gradient will, therefore, depend on the ratio of the coefficient of ordinary diffusion D_{12} to a certain coefficient of thermal diffusion D_t. This ratio will be denoted k_t and will be an indication of the thermal diffusion which will actually take place.

To prove the existence of this phenomenon, Chapman and Dootson[26], carried out a series of experiments using a very simple form of apparatus. A mixture of two gases of different molecular weights, e.g., CO_2 and H_2, was introduced into two glass bulbs which were connected to each other and which were maintained at different temperatures. After a few hours, the gas mixture

from each bulb was analysed. The results clearly indicated that thermal diffusion had taken place, although to a far less extent than that predicted on theoretical grounds.

Later, Ibbs[27], carried out a more detailed investigation of thermal diffusion in gases using a more elaborate apparatus and a more refined technique. His results proved conclusively that the phenomenon did take place, that maximum separation due to thermal diffusion is obtained when the gases are mixed in nearly equal proportions by volume and that the amount of separation varies with log T_1/T_2, where T_1 and T_2 are the absolute temperatures forming the temperature gradient.

Gillespie[28] puts Chapman's approximate formula for thermal diffusion in a binary mixture in the form:

$$k_t = \frac{dx_1}{d\ln T} = \frac{A\,x_1 + B\,x_2}{1 + C\,x_1/x_2 + D\,x_2/x_1} \qquad (17)$$

where T is absolute temperature, x mole fraction and the coefficients A, B, C and D are functions of the molecular weights and the ratios of the diameters. He derived a simple formula for thermal diffusion in which no account is taken of the size of the molecules or their mutual forces but which is based solely on molecular weight which is the most important variable. In the case where there are/

are two species only the equation will be:

$$k_t = \frac{dx_1}{d\ln T} = \frac{x_2 x_1 (m_2 - m_1)}{2 (m_1 x_1 + m_2 x_2)} \qquad (18)$$

where m_1 and m_2 are the square roots of the molecular weights.

Gillespie compared the values of theoretical separation as calculated from equations (17) and (18) with those obtained experimentally by several workers for binary gaseous mixtures. This comparison clearly indicated that equation (18), apart from being simpler to use, gave considerably better agreement than equation (17). It was found, however, that the calculated values of thermal diffusion were almost invariably higher than the observed values, one exception being the case where hydrogen was one of the components of the binary system. It was found that in this case the rule does not necessarily hold and the observed values might exceed the calculated values. It will be safe, therefore, to accept equation (18) as an indication of the possible extent of thermal diffusion in a binary mixture. The most obvious conclusions to be drawn from equation (18) are that thermal diffusion will not take place should m_1 and m_2 be equal, that it will increase as the difference between the molecular weights of the two gases increases, and that thermal diffusion/

diffusion for any two particular gases will reach a maximum when their molar fractions are equal.

Work on equilibria involving gaseous and solid phases was pioneered by Sainte-Claire Deville[29] in 1870. He was the first to determine the H_2O:H_2 ratio in equilibrium with metallic iron and FeO, his determinations being done on a static gaseous system in contact with a mixture of Fe and FeO at different temperatures. Several later workers, using the same type of apparatus as that used by Deville, obtained equilibrium ratios covering a considerable range of values; for a given temperature, some being as much as 40% higher than others.

Using a dynamic rather than a static type of apparatus, Emmet and Schultz[30] obtained values for the constants K_1 and K_2 of the reactions;

$$FeO + H_2 = Fe + H_2O \quad ; \quad K_1 = \frac{H_2O}{H_2}$$

and $$Fe_3O_4 + H_2 = 3\ FeO + H_2O \quad ; \quad K_2 = \frac{H_2O}{H_2}$$

that were consistent among themselves and agreed with the values calculated indirectly from the Fe - C - O system[31] and the equilibrium constant K_3[32] for the reaction;

$$CO_2 + H_2 = CO + H_2O \quad ; \quad K_3 = \frac{(H_2O)(CO)}{(CO_2)(H_2)}$$

but/

but which showed a 40% discrepancy when compared with values obtained by the carefully performed static experiments. To account for this considerable persistent difference in results given by the two types of apparatus a detailed study of all possible sources of error was made. The conclusion was that the reported values of K_1 and K_2 obtained by the use of a flow system are essentially correct and that the 40% discrepancy is to be attributed to an error caused by thermal diffusion in practically all previous static experiments. This conclusion was arrived at after an experiment conducted in the static type apparatus[33] showed that the H_2O:H_2 ratio at the cold end was 40-48% higher than that at the hot end of the apparatus.

Even when CO_2- CO mixtures are used, thermal diffusion measurements of Ibbs and Underwood[34] had indicated that if equilibrium with respect to thermal diffusion were established the 'cold end' CO_2:CO ratios for the Fe-FeO system might be higher than the 'hot end' values by 6.3% at 600°C and 7.9% at 1000°C. It should be pointed out that these values should be regarded as being the maximum possible. Darken and Gurry[35] in their work on the same system were able to out down thermal diffusion to 0.25% of the CO_2:CO ratio by carefully regulating the rate/

rate of gas flow through the system.

Chipman[36] in 1933, studied the reaction between water vapour-hydrogen mixtures and liquid iron, using an induction furnace for the purpose. This method of heating although ideal in many ways introduces a very sharp temperature gradient at the surface of the melt. The results obtained by Emmet and Schultz[33] &[37] made Chipman and Fontana[38] suspect the possibility of thermal diffusion being responsible for the introduction of a serious error in Chipman's earlier results. Their suspicions were heightened by the fact that for a given oxygen content of liquid iron the observed $H_2O:H_2$ ratio was consistently higher than that calculated from the ratio $CO_2:CO$ found by Vacher and Hamilton[39]. This led Chipman and Fontana[38] &[40] to repeat the equilibrium determinations using a form of apparatus which allowed the gas stream to be preheated to as near the temperature of liquid iron as possible before coming into contact with it. The results showed that :

$K = \frac{pH_2O}{pH_2 \times \%O}$ at 1600°C and 0.065 %O in the liquid iron

was 21% higher when no preheat was used. The most recent work done on this system by Dastur and Chipman[41], in which a most efficient method of preheating the gas stream/

stream was used, showed that the effect was even greater, values of K for runs with no preheat being 31% higher than those where an efficient preheat was used.

It is worthy of note that the H_2O:H_2 ratios for a given oxygen content in liquid iron at a given temperature where an efficient preheat was given to the gas stream agree remarkably with calculated values from the ratio CO_2:CO found by Vacher and Hamilton[39]. This seems to indicate that in a CO_2- CO system little thermal diffusion takes place as compared to that which takes place in H_2O - H_2 systems. This is in agreement with equation (18) and is to be expected, since the ratio of the molecular weight of CO_2 to that of CO is 1.53 as compared to a ratio of 9 in the case of an H_2O - H_2 system.

It could be safely assumed, therefore, that thermal diffusion will not take place to any great extent in the system SO_2-N_2 where the ratio of the molecular weight of SO_2 to that of N_2 is 2.38, i.e., approximately one fourth of the ratio in the case of an H_2O-H_2 system.

Another factor which leads to the same assumption with respect to the present work is the fact that the percentage of SO_2 in the SO_2-N_2 mixtures never exceeded 7%, and, according to equation (18), there will be 6.5 times more thermal diffusion when the SO_2:N_2 ratio is 50:50 than when the ratio is 5:95.

CHAPTER IV.

Discussion of Results and Conclusions.

The results obtained from a study of the reaction between molten iron and sulphur dioxide, given in Table (3) and shown graphically in Figs. (12) and (18), indicate that a linear relationship exists between the partial pressure of sulphur dioxide and the sulphur content of the molten iron, when sufficient time is allowed for the attainment of steady state conditions. Fig. (18) also shows clearly the effect of temperature, low temperatures encouraging the pick up of sulphur by liquid iron from the gas mixture. The relationship between $[S]$, pSO_2 and temperature shown graphically in Fig. (18) can be expressed mathematically as follows:-

$$\log \frac{[S]}{pSO_2} = \frac{2642}{T} + 0.233 \qquad (19)$$

The applicability of such an expression to the results obtained might lead one to suspect that true thermodynamic equilibrium existed between gas and metal. This is contrary both to other observed facts and to the known thermodynamic data on the reactions likely to occur between liquid iron and sulphur dioxide.

Two important facts were noted in all the experiments performed. Firstly, that vigorous oxidation of the/

the metal by the sulphur dioxide always occured throughout each experiment. The metal eventually became saturated with oxygen (as was shown by the analyses for oxygen) when an oxide phase separated out and was absorbed by the crucible. This caused blackening of the crucible and eventual failure. A certain amount of iron sulphide was also partitioned into the oxide phase and was found by chemical analysis to be present in the crucible walls. The second point of interest was that sulphur vapour was formed during the reaction between metal and gas in all the experiments using a gaseous atmosphere of sulphur dioxide and nitrogen. The sulphur vapour was easily detectable in the exit gases. The probable reaction occuring being:

$$2Fe_{(liq.)} + SO_2 = \underset{(slag)}{2FeO} + \tfrac{1}{2}S_{2(gas)} \qquad (20)$$

The free energy change for this reaction has been calculated to be:

$$\Delta G^{o} = -24,725 + 4.42\ T$$

The fact that elemental sulphur does not appear in the exit gases when free oxygen is present in the gas phase does not mean that reaction (20) no longer occurs. The explanation is that the sulphur recombines with the free oxygen in the gas mixture, after it leaves the metal surface, but while still in the hot zone of the furnace.

It/

It is evident, therefore, that several chemical reactions may be occuring simultaneously, and that the constancy of composition ultimately reached by the metal is due to the attainment of steady state conditions within the system, and not to a condition of thermodynamic equilibrium between gas, metal and slag. True equilibrium between gas and metal is never attained, and if gas were passed for a sufficient length of time, complete conversion of the iron to iron sulphide and iron oxide would occur, provided that the crucible would withstand the chemical attack over such a prolonged period.

Maurer and Bischof[17] used the following equation to explain the reaction between liquid iron and sulphur dioxide:-

$$Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2 \qquad (6)$$

Chipman and Ta Li[19] pointed out that should equation (6) represent the controlling reaction between sulphur dioxide and molten iron, then from a calculation based on the free energy change of the reaction, no sulphur pick up should occur above 0.00015% FeS when liquid iron is in contact with a gas mixture containing equal volumes of sulphur dioxide and oxygen at 1535°C, any sulphur in excess being oxidised to sulphur dioxide. It is evident that this equation does not adequately describe the reaction taking place./

place. A calculation of the free energy change of this reaction ($\Delta G^{\circ}_{1650^{\circ}C.} = 30,605$) confirms this conclusion. Other reactions with a more probable free energy change are more likely to occur, as for instance, the one cited by Chipman and Ta Li:-

$$3Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + \underset{(metal)}{2FeO} \qquad (15)$$

Using the most recent data, the free energy change for this reaction has been calculated to be:

$$\Delta G^{\circ} = - 19,746 - 11.15\ T$$

at 1650°C $\Delta G^{\circ} = - 41,187$

The discrepancy between the results theoretically expected from reaction (15) and those actually obtained is shown in Table(6).

Table(6).

p_{SO_2}	[FeS] obs.	[FeS] calc.	$\frac{[FeS]\ calc.}{[FeS]\ obs.}$
	Temperature 1650°C.	$K = 4.78 \times 10^4$	
0.02	2.144	742.5	346
0.04	4.565	1714.0	375
0.06	7.040	3040.0	432
	Temperature 1750°C.	$K = 3.71 \times 10^4$	
0.02	1.540	266.0	173
0.04	3.847	604.0	157
0.06	6.185	1033.0	167

It/

It is apparent that [FeS] calc. is approximately 380 times [FeS] obs. at 1650°C and 160 at 1750°C. Obviously, equilibrium has not been attained in this reaction.

It may appear strange that although the equilibrium percentage of sulphur in the metal is impossibly high, the limit of sulphur in the metal actually reached was so very far removed from this value. An analysis of the reactions occuring may give a fuller quantitative picture.

In the early stages, the following reactions occur simultaneously between gas and metal:

(a) $2Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \frac{1}{2}S_{2(gas)}$

(b) $3Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \underset{(metal)}{FeS}$

(c) $Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2$

Of these, reaction (c) is probably very slow, and the oxygen formed would be expected to combine immediately with iron to form ferrous oxide:-

(d) $2Fe_{(liq.)} + O_2 = \underset{(metal)}{2FeO}$

The net result of (c) and (d) being (b); reaction (c) could, therefore, be neglected.

The ferrous oxide formed, at first enters the metal, until the latter is saturated, when a separate slag phase containing iron oxide is formed. Ferrous sulphide will also/

also enter the slag phase by partition from the metal, and when the steady state conditions are reached, the rate of formation of iron sulphide and iron oxide from metal and gas by reactions (a) and (b) must be exactly equal to the rate of transfer of iron sulphide and iron oxide to the slag phase.

If the rates of the forward and backward reactions in the following equations are as indicated:-

(a) $$2Fe_{(liq.)} + SO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2FeO_{(metal)} + \tfrac{1}{2}S_{2(gas)}$$

(b) $$3Fe_{(liq.)} + SO_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2FeO_{(metal)} + FeS_{(metal)}$$

then when the steady state condition is reached, the rate of formation of FeS from metal and gas, and therefore the rate of transfer of FeS to slag is given by:-

$$k_1[Fe]^3 p_{SO_2} - k_2[FeS][FeO]^2 = k_1 p_{SO_2} - k_2[FeS][FeO]^2$$

$$= k_1 p_{SO_2}\left(1 - \frac{1}{K_1} \cdot \frac{[FeS][FeO]^2}{p_{SO_2}}\right)$$

where K_1 is the equilibrium constant for reaction (b), i.e., the value of $\dfrac{[FeS][FeO]^2}{pSO_2}$ at equilibrium. Similarly the rate of formation of FeO from metal and gas, and therefore the rate of transfer of FeO to slag is given by:-

$$2(k_1 p_{SO_2} - k_2[FeS][FeO]^2 + k_3 p_{SO_2} - k_4[FeO]^2 p_{S_2}^{\frac{1}{2}})$$

=/

$$= 2\, p_{SO_2} \left[k_1 \left(1 - \frac{1}{K_1} \cdot \frac{[FeS][FeO]^2}{p_{SO_2}}\right) + k_3 \left(1 - \frac{1}{K_2} \cdot \frac{[FeO]^2\, p^{\frac{1}{2}}_{S_2}}{p_{SO_2}}\right)\right]$$

where K_2 is the equilibrium constant for reaction (a), i.e., the value of $\frac{[FeO]^2\, p^{\frac{1}{2}}_{S_2}}{p_{SO_2}}$ at equilibrium.

It is apparent that when $\frac{[FeS][FeO]^2}{p_{SO_2}} = K_1$ and $\frac{[FeO]^2\, p^{\frac{1}{2}}_{S_2}}{p_{SO_2}} = K_2$, the rate of formation of iron sulphide and iron oxide as a slag phase will be zero and true equilibrium would exist between metal and gas.

It is clear that unless many simplifying assumptions are made regarding the relative rates of the various reactions, and in the absence of suitable slag analyses, little further can be gained from a study of the reaction kinetics of this system, because of the numerous variables involved. It does not help in explaining why, although equilibrium is never reached, a linear relationship exists between the sulphur content of the metal and the partial pressure of sulphur dioxide in the gas phase, nor does it explain why an 'apparent equilibrium constant' can be obtained from the experimental data many times larger than the true equilibrium constant. All possible sources of experimental error have been discussed in Chapter II and it can be concluded that such a large discrepancy could not/

not possibly be due to any such errors. It does seem a possibility, however, in view of the relationship shown graphically in Fig.(18) and expressed mathematically by equation (19) that equilibrium is reached or almost reached in one of the intermediate reactions involved in the formation of iron sulphide.

The following consideration of the individual reactions leading to the formation of iron sulphide and iron oxide may help in clarifying the issues involved, although a complete solution has not been obtained owing to the complexity of the problem and the lack of certain data.

The experimental observations and results suggest that the reactions which lead to the formation of FeO are very fast compared with those leading to the formation of FeS. Sulphur and oxygen can enter the metal by either of the following pairs of reactions:-

1a. $2Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \frac{1}{2}S_{2(gas)}$

1b. $Fe_{(liq.)} + \frac{1}{2}S_{2(gas)} = \underset{(metal)}{FeS}$

2a. $Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2$

2b. $2Fe_{(liq.)} + O_2 = \underset{(metal)}{2FeO}$

or simultaneously by the reaction:-

3./

3. $3Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \underset{(metal)}{FeS}$

It is fairly certain, therefore, that reaction (2a) is very slow compared with (1a), and that most of the sulphur dioxide reacts with iron according to (1a). Sulphur would then enter the metal by reaction (1b), i.e., by reaction of the metal with sulphur vapour, although this does not result in complete combination with the sulphur vapour, and much of it escapes with the exit gases*.

---

* Complete combination, however, is not restricted by any slowness of reaction (1b), as shown by Fig. (13) showing the effect of time on the reaction between gas and metal, and by the results of experiment 'K-1' and 'K-2', in which the final position was approached from the high sulphur (in metal) side. In each of these experiments, the sulphur content of the metal dropped, though not as far as the sulphur percentage obtained by passing sulphur dioxide over molten iron in the normal way. This is to be expected, since, as there is no mechanism available for removal of sulphur from the metal to the gas phase, the excess sulphur can only be removed to the slag phase by iron oxide formed from the reaction of the metal and sulphur dioxide. This method of sulphur removal is a relatively slow process as the amount of iron oxide formed is limited by the supply of oxygen from sulphur dioxide in the gas phase. A simple calculation based on the percentage of sulphur dioxide used and the rate of gas flow indicated that the fall in sulphur content was of the order expected.

It was, of course, impossible to measure the partial pressure of sulphur vapour at the gas-metal interface but an approximation may be made by assuming the equilibrium values for P_{SO_2} and P_{S_2} at the gas-metal interface in the reaction:-/

reaction:-

$$2Fe_{(liq.)} + SO_2 = \underset{(slag)}{2FeO} + \tfrac{1}{2}S_2 \qquad (20)$$

are approached, because of the rapidity of this reaction compared with the other reactions taking place. Using the partial pressures of sulphur vapour calculated therefrom, the sulphur contents to be expected in the molten metal if equilibrium were to be reached in the reaction:-

$$Fe_{(liq.)} + \tfrac{1}{2}S_2 = \underset{(metal)}{FeS} \qquad (21)$$

for which, $\triangle G^{\circ} = -42,526 + 9.05\ T$

have been calculated and are compared with the values actually observed in Table(7).

TABLE(7).

P_{SO_2}	[FeS] obs.	[FeS] calc.	$\frac{[FeS]\ calc.}{[FeS]\ obs.}$
Temperature 1650°C.		$K_{20} = 69.82$	$K_{21} = 721.0$
0.02	2.144	69.6	32.4
0.04	4.565	99.4	21.8
0.06	7.040	122.4	17.4
Temperature 1750°C.		$K_{20} = 50.82$	$K_{21} = 411.0$
0.02	1.540	39.0	25.3
0.04	3.847	56.2	14.6
0.06	6.185	69.2	11.2

These values represent the maximum sulphur contents possible on the basis of the above series of reactions. They are still much higher than those actually obtained, but are far better than those calculated from reaction(15).

The actual values obtained should approach the calculated values, the nearness of approach being dependent on the relative rates of reaction (1b) and the rate at which sulphur passes from metal to slag. If the latter were very slow, the actual sulphur contents should approach very closely to the "equilibrium" values.

The three reactions involved in sulphide formation are therefore:-

$$2Fe_{(liq.)} + SO_2 = \underset{(slag)}{2FeO} + \tfrac{1}{2}S_{2(gas)} \qquad (20)$$

$$Fe_{(liq.)} + \tfrac{1}{2}S_{2(gas)} = \underset{(metal)}{FeS} \qquad (21)$$

$$\underset{(metal)}{FeS} = \underset{(slag)}{FeS} \qquad (22)$$

It is apparent that if reactions (20) and (21) are rapid and reaction (22) slow, equilibrium may be attained in reaction (21) even though the system as a whole is not in equilibrium. It is impossible to state how closely reaction (21) approaches equilibrium from the results obtained, but either reaction (22) is not abnormally slow compared with (20) and (21), or other factors must be found to account for the difference between the observed sulphur/

sulphur values and those calculated assuming (22) to be a very slow reaction (i.e., those given in columns 2 and 3 of Table(7). One such factor is the activity of sulphur in iron containing both oxygen and sulphur. It is known that the activity of sulphur is affected by the presence of other elements dissolved in the iron. Thus, Morris and Williams[24] studied the effect of silicon and found that the activity coefficient of sulphur was almost doubled by the presence of 4% silicon, and increased five or six fold by 9% silicon. Kitchner, Bockris and Liberman[42] have similarly shown that saturation of iron with carbon approximately doubles the activity of sulphur. If saturation of iron with oxygen results in an increase in the activity of sulphur, this would partially account for the differences in values observed.

A further possibility is that the thermodynamic data used in the above calcutations may not be sufficiently accurate. Thus the accepted margin of error[43] in the free energy change for each of the reactions:-

$$SO_2 = \tfrac{1}{2}S_2 + O_2$$

$$2Fe_{(liq.)} + O_2 = 2FeO_{(slag)}$$

which in turn were used to calculate the free energy change for the reaction:-

$$2Fe_{(liq.)} + SO_2 = 2FeO_{(slag)} + \tfrac{1}{2}S_2 \qquad (20)$$

is/

is ± 3 Kg.Cals. A total error of 6 Kg.Cals. would increase the ratio $[FeS]_{calc.} : [FeS]_{obs.}$ by about 4.8. Whereas the error is not likely to be as great as 6 Kg.-Cals., the possibility of such an error cannot be ignored.

The system may therefore be considered as one consisting of liquid iron containing sulphur and saturated with oxygen, reacting with sulphur dioxide to form liquid ferrous oxide and sulphur vapour. The sulphur dissolved in iron approaches equilibrium with the sulphur vapour, but some of the iron sulphide formed is being continuously partitioned into the slag phase along with ferrous oxide formed by reaction (1a), according to equation(22):-

$$\underset{(metal)}{FeS} = \underset{(slag)}{FeS}$$

at equilibrium, $$L_{FeS} = \frac{(FeS)}{[FeS]}$$

when, according to Bardenheur and Geller[18] the distribution coefficient L_{FeS} is given by:

$$\log L_{FeS} = \frac{2390}{T} - 0.714 \qquad (23)$$

Fig.(20) shows the relationship actually observed between iron sulphide in metal and slag, based on the metal and slag analyses given in Table(5). It will be noted that,

$$\frac{(FeS)}{[FeS]} = 1.60 \quad @ \quad 1650^{o}C.$$

and/

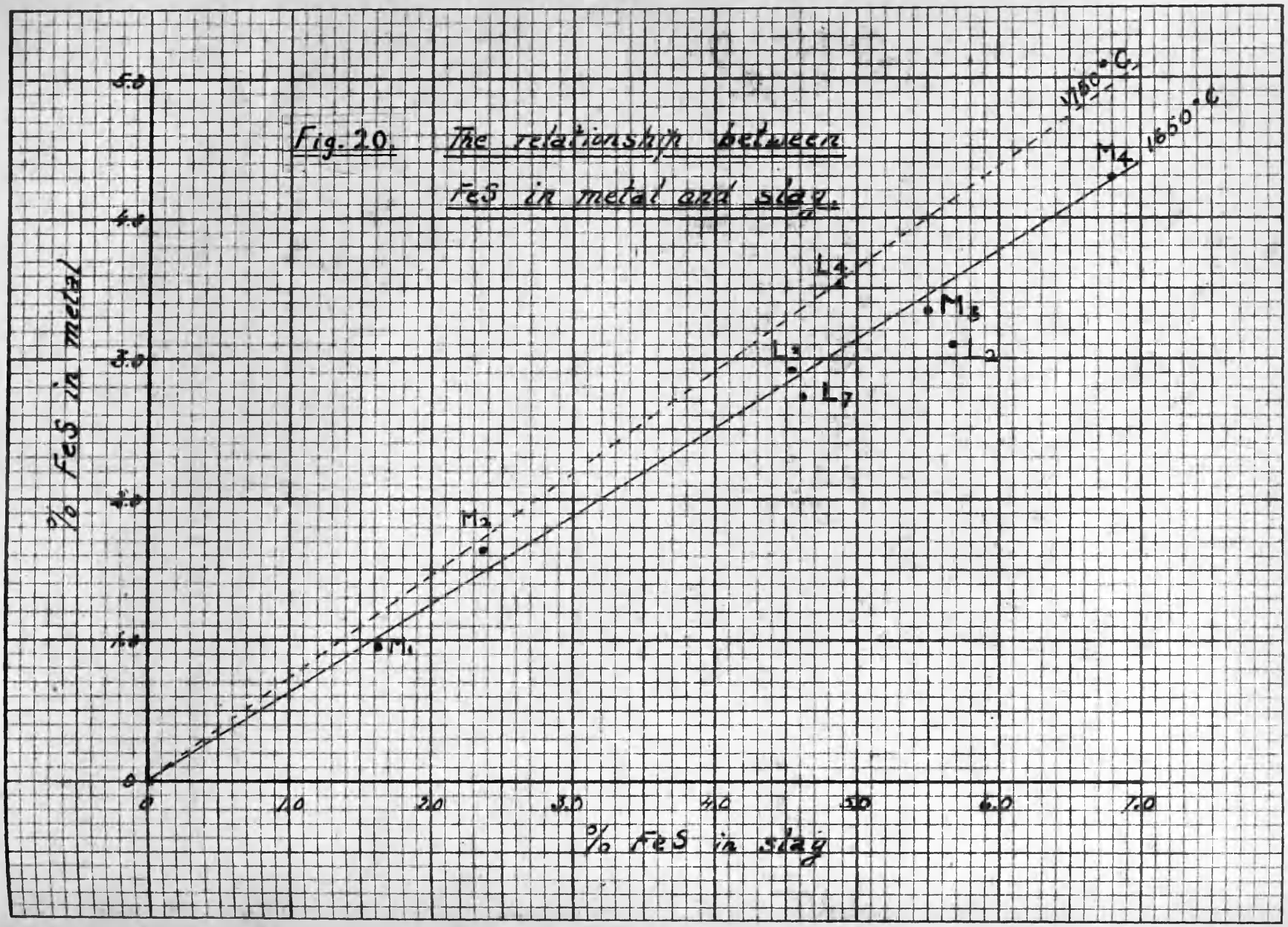


Fig. 20. The relationship between FeS in metal and slag.
% FeS in metal
% FeS in slag
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1750°C
1650°C
M4
L4
M3
L3
L2
L1
M2
M1

and $$\frac{(FeS)}{[FeS]} = 1.37 \quad @ \quad 1750^{o}C.$$

whereas the equilibrium values from equation (23) are:

$$L_{FeS} = 3.38 \quad @ \quad 1650^{o}C.$$

and $$L_{FeS} = 2.93 \quad @ \quad 1750^{o}C.$$

i.e., approximately twice those obtained in the present investigation. Since there is no reason to doubt the validity of the results of Bardenheur and Geller, it is to be concluded that equilibrium between metal and slag is not achieved in the above experiments. This is not surprising in view of the very rapid rate of formation of FeO.

On the basis of the above explanation of the reactions taking place between molten iron and sulphur dioxide, it would be expected that the presence of oxygen in the gas phase would not greatly affect the final metal sulphur contents attained if the approach to equilibrium in reaction (1b) were fairly close. If removal of sulphur from metal to slag were a rapid process, and the approach to equilibrium in reaction (1b) be fairly remote, then oxygen in the gas phase would be expected to lower the observed metal sulphur content still further. Table(5) gives the results obtained using from one to six percent oxygen in the gas mixture, and the superposing of the isothermal lines of Fig.(18), where oxygen was absent, on Fig.(19), based on

these/

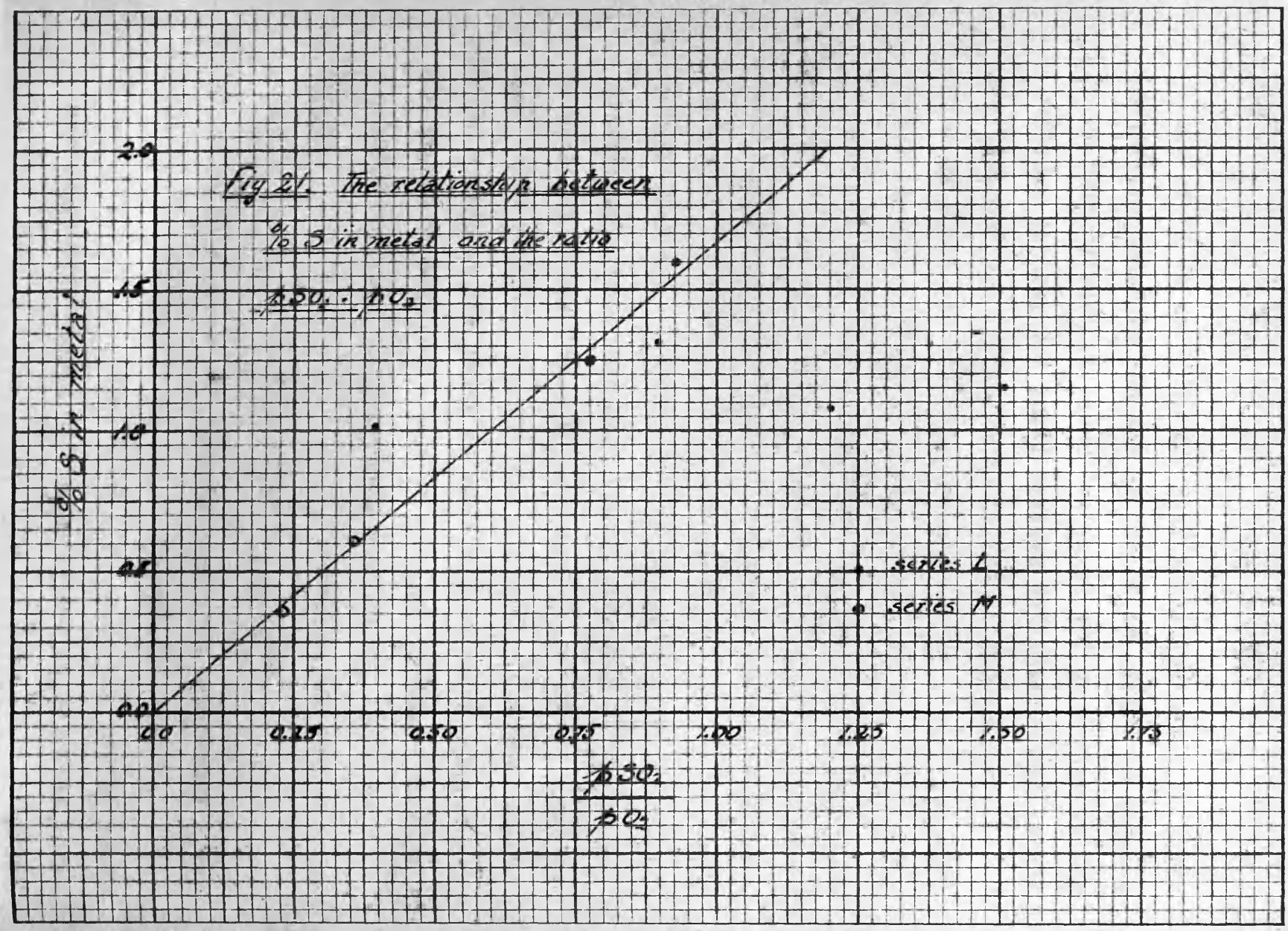


Fig 21. The relationship between
% S in metal and the ratio
% SO3 / % O2
% S in metal
2.0
1.5
1.0
0.5
0.0
0.0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
% SO3 / % O2
series L
series M

these results, indicates that the addition of up to six percent by volume of oxygen to the gas mixture apparently has no effect on the resultant metal sulphur content attained; the controlling factors being the partial pressure of sulphur dioxide in the gas mixture and the temperature. This conclusion is further supported by Fig. (21), in which the sulphur content of the metal is plotted against the ratio $P_{SO_2}:P_{O_2}$. It may be noted that in Fig. (21) the points representing the results obtained in series "M" fall a straight line. This not because any relationship exists between [S] and the ratio $P_{SO_2}:P_{O_2}$, but because in series "M" the value of P_{O_2} was kept almost constant and, therefore, the values of $P_{SO_2}:P_{O_2}$ in all four runs were proportional to P_{SO_2}. The points representing the results obtained in series "L", where P_{SO_2} was kept fairly constant while P_{O_2} was varied, show clearly that no relationship exists between [S] and the ratio $P_{SO_2}:P_{O_2}$ as was postulated by Maurer and Bischof[17]. It follows also that the reaction between molten iron and oxygen:-

$$2Fe_{(liq.)} + O_2 = 2FeO$$

is a very rapid one, and possibly the most rapid reaction of all. Thus at the gas metal interface the oxygen potential of the gas phase will be very rapidly brought down to that which is in equilibrium with liquid iron saturated with/

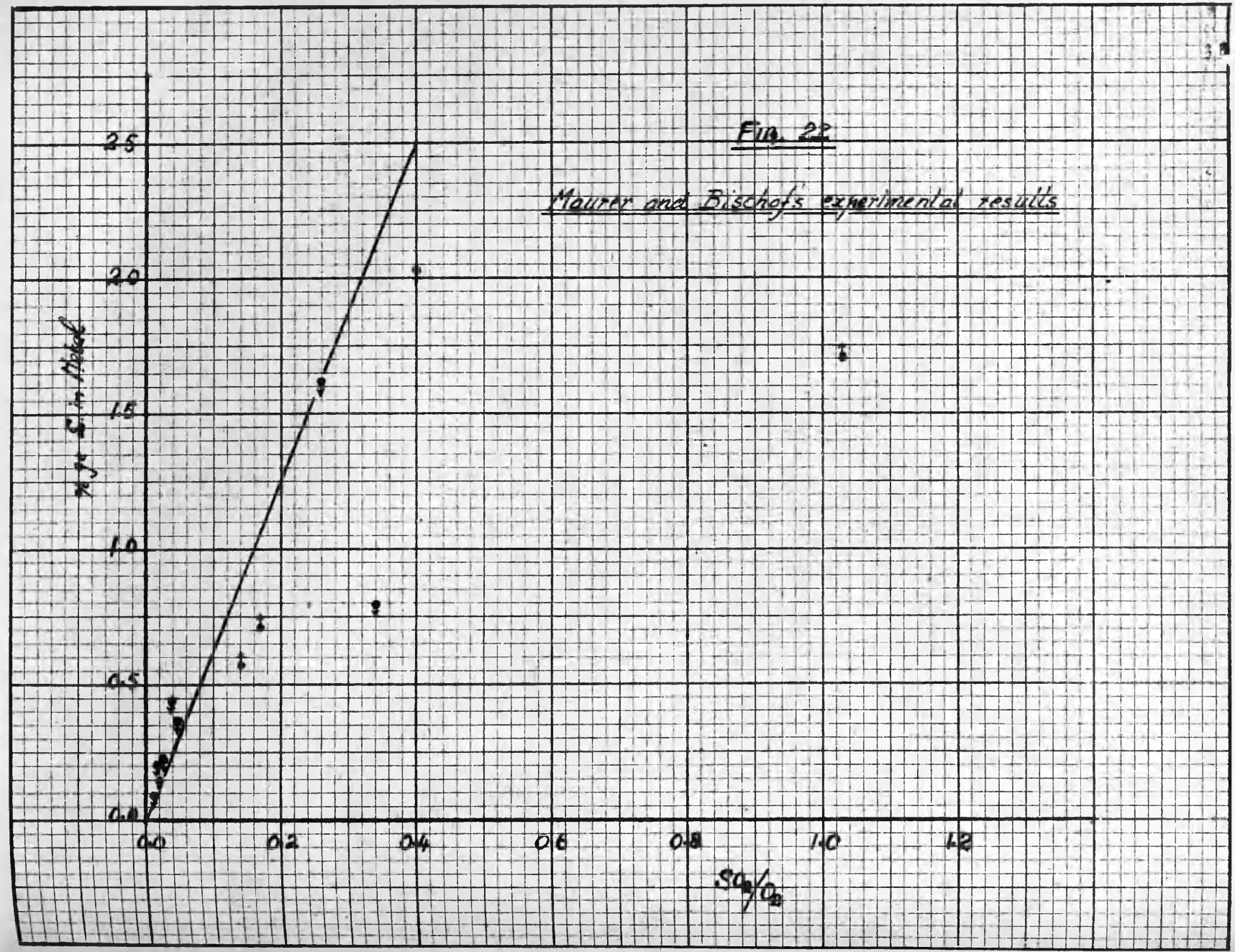


Fig. 22
Maurer and Bischof's experimental results
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
SO_2/O_2

with iron oxide, or with the slag phase which is being continuously formed. In other words, it reacts preferentially with molten iron rather than the sulphur vapour formed by reaction (1a), and therefore does not directly affect the sulphur content of the metal. It is evident, therefore, that the interpretation of their results by Maurer and Bischof in the form of a proportionality between $[S]$ and $P_{SO_2}:P_{O_2}$ is erroneous.

Because of the results obtained from series "L" and "M", and the conclusions arrived at above, it was decided to replot the results obtained by Maurer and Bischof in in their work on the reaction between liquid iron and mixtures of oxygen and sulphur dioxide, in the same manner in which the present results have been plotted (i.e., plotting $[S]$ against P_{SO_2}). Only the lower metal sulphur content runs of Maurer and Bischof have been considered, i.e., metal sulphur contents ranging from 0.096% to 2.04%. In these cases the oxygen content of the gas ranged from 1.5% to 15.5% by volume. The high sulphur content runs, which ranged from about 7.0% to about 30.0% sulphur were not considered, since their sulphur content is far higher than the range studied in this work. Fig.(22) shows the relationship obtained by Maurer and Bischof, while that obtained by replotting their results is shown in Fig.(23). It/

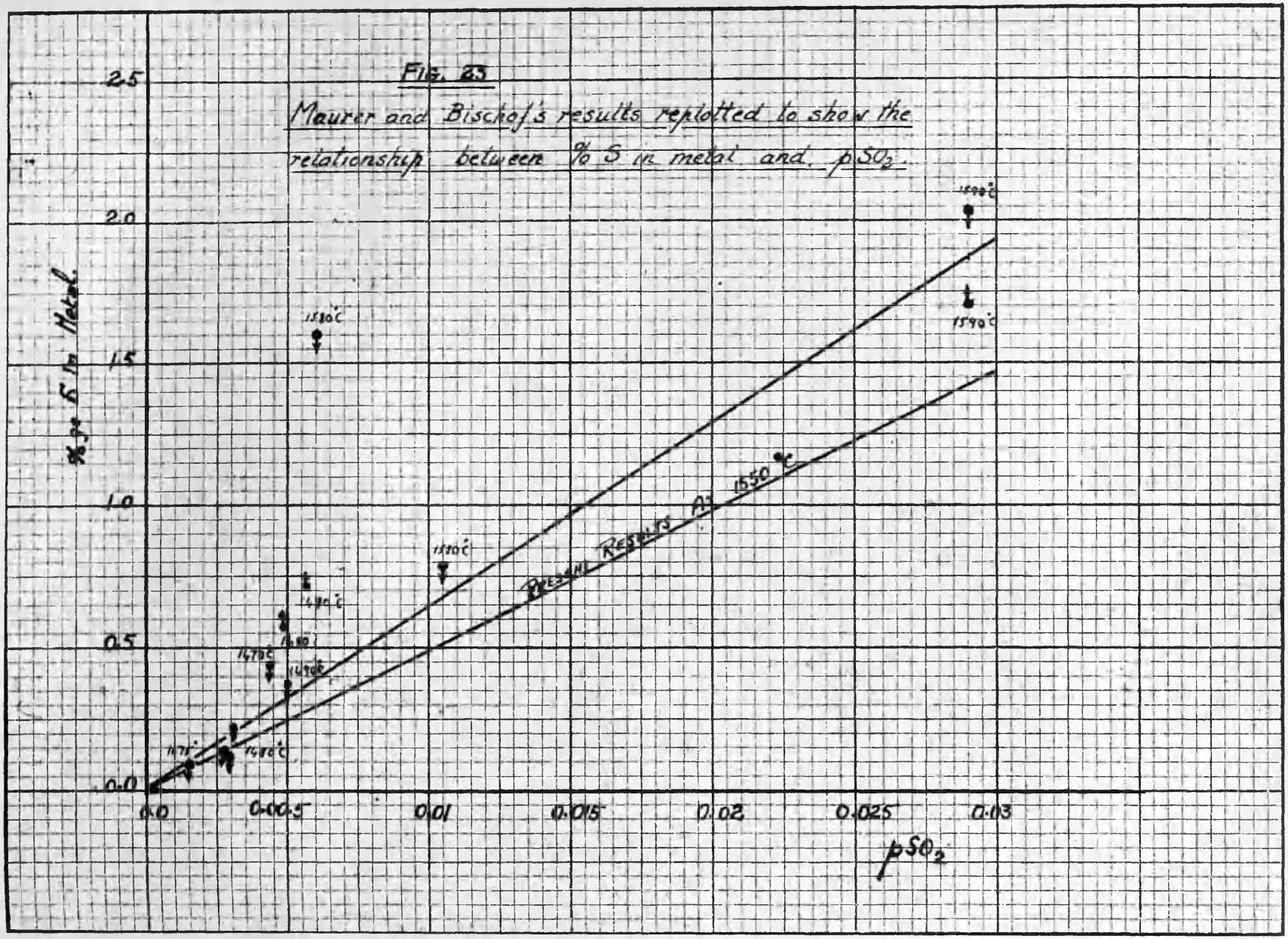


Fig. 23
Maurer and Bischof's results replotted to show the relationship between % S in metal and pSO_2.
% S in Metal
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.005
0.01
0.015
0.02
0.025
0.03
pSO_2
1590°C
1540°C
1580°C
1550°C
1490°C
1480°C
1470°C
1490°C
1475°C
1480°C
Present Results At 1550°C

It can be seen that good agreement is obtained with the conclusions arrived at above and with the results obtained in the present work for 1550°C. The discrepancy between the two lines in Fig. (23) is probably due to imperfect technique in the experimental work of Maurer and Bischof, especially with regards to gas circulation and sampling.

It should be mentioned here that although the investigation of the reaction between sulphur dioxide and liquid iron in the presence of oxygen was restricted to oxygen contents in the gas phase of the order of six per cent by volume for reasons given earlier (see page 64), there is no reason to expect results widely different from those obtained in series "L" and "M", should a higher oxygen content be present.

The above work has not produced any new thermodynamic data on the reaction between liquid iron and sulphur dioxide, but it has established the boundaries of the region of liquid immiscibility, for the temperatures investigated, in the ternary diagram Fe-O-S. The relationship between the sulphur and oxygen contents of the metal for 1650°C and 1750°C are shown graphically in Fig. (24). The lines AB and A'B' when extrapolated to zero sulphur content in the metal at C and C' respectively, indicate oxygen contents which compare favourably with the saturation values of/

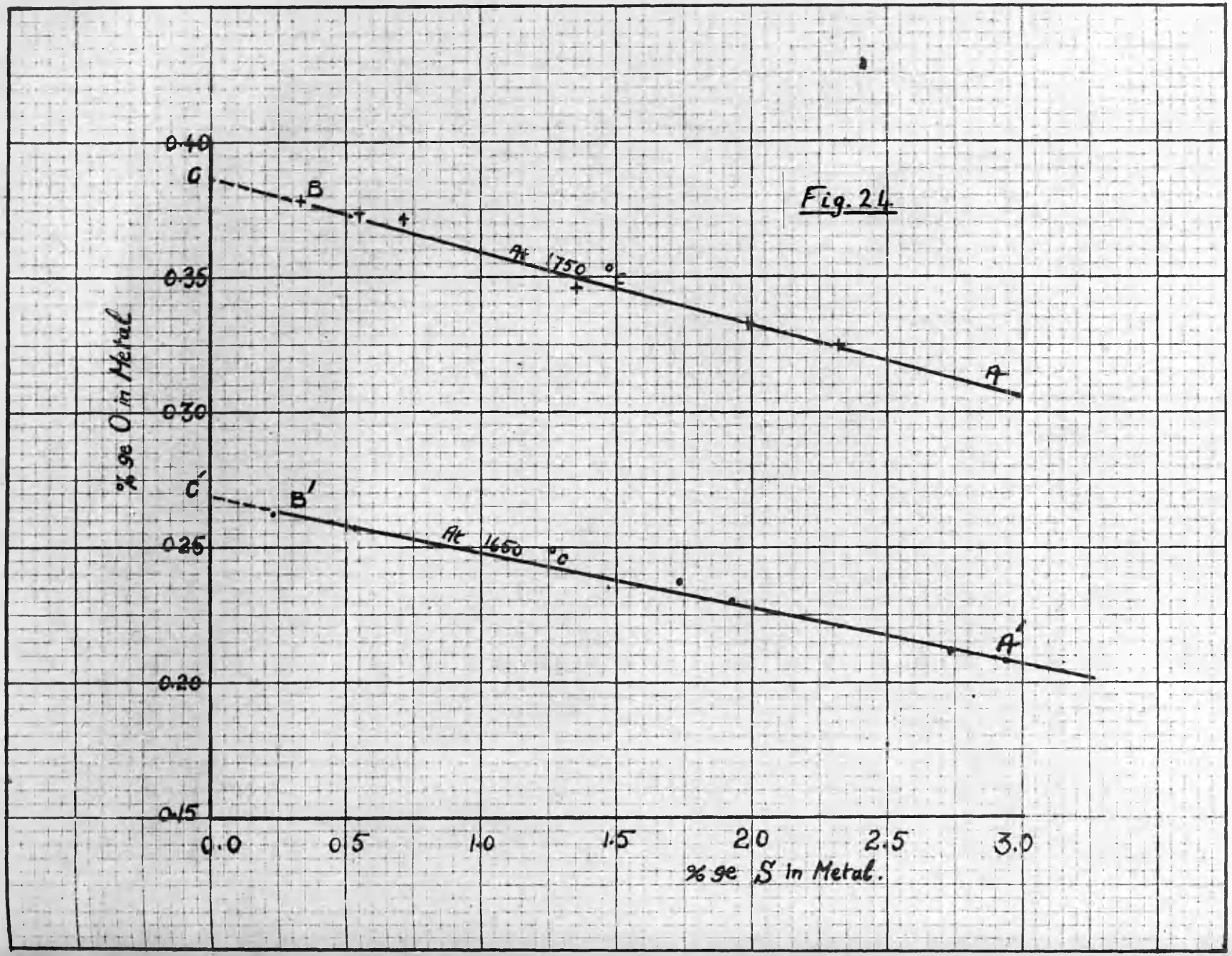


Fig. 24
0.40
0.35
0.30
0.25
0.20
0.15
C
B
A
At 1750 °C
C'
B'
A'
At 1650 °C
% ge O in Metal
0.0
0.5
1.0
1.5
2.0
2.5
3.0
% ge S in Metal.

of iron with ferrous oxide, at the same temperatures, obtained by Taylor and Chipman[21]. The observed oxygen contents at zero sulphur were 0.386% @ 1750°C and 0.267% @ 1650°C., as compared with the solubility limits calculated from the results of Taylor and Chipman of 0.408% @ 1750°C and 0.281% @ 1650°C. This close similarity confirms the reliability of the oxygen determinations carried out in this work. Furthermore, it is significant to note that the difference between the observed and calculated oxygen contents of liquid iron saturated with FeO, viz., 0.022% @ 1750°C and 0.012% @ 1650°C, corresponds to the evolution of 6 ml. sulphur dioxide at 1750°C, and 3.5 ml. at 1650°C from a 20 gm. ingot. Gas evolution was observed to occur during solidification and it was also observed that the volume of gas evolved, (which, as was shown on page 62, could only be sulphur dioxide) increased with the temperature of the melts. The lines A B and A'B' in Fig. (24) may, therefore, lie slightly higher than indicated. These lines actually represent the limits of solubility of the oxide-sulphide phase in liquid iron at the corresponding temperatures, in the Fe-O-S ternary diagram referred to above, and are redrawn as such in Fig. (25).* As these lines are almost parallel, a third line X X' can be drawn from X (the monotectic point in the binary diagram

*Fig. (25) will be found inside back cover.

Fe-O) parallel to them, representing the intersection of the limit of the two-liquid phase field with the liquidus surface, thus corresponding to equilibrium between δ iron, liquid iron and the liquid iron oxide-iron sulphide phase. This supposes that the temperature drop along X X' from the Fe-O side of the ternary diagram is small, an assumption which is reasonably justified in view of the small temperature drop along the corresponding line in similar diagrams, e.g., the Fe-C-O diagram.

It has been mentioned earlier that in all the cases investigated in the present work the liquid iron became saturated with a second liquid phase consisting mainly of ferrous oxide. The compositions in each case would not necessarily lie on the FeO-FeS join, so that strictly speaking they cannot be described in terms of FeO and FeS only, as was done in Table(5), but the analyses indicated that the compositions lay sufficiently close to the FeO-FeS join to warrant this simplification. The points corresponding to these slag compositions, and the conodes connecting them with the corresponding metal compositions have not been plotted on the ternary diagram, because of the large scale required, but the relationships involved are summarised in Table(8).

TABLE(8)/

TABLE(8).

Temp. °C.	Metal analysis.		Slag analysis.	
	%S	%O	%FeS	%FeO
1745	1.317	0.350	4.88	95.12
1650	1.603	0.235	6.80	93.20
1650	1.083	0.246	4.54	95.46
1645	1.248	0.243	5.51	94.49
1645	0.358	0.261	1.62	98.38
~1620	0.610	~0.227	2.37	97.63
~1610	1.021	~0.209	4.61	95.39

The results of the present work can also be used to calculate the most suitable furnace atmosphere for minimising sulphur pick-up in open-hearth steelmaking. The saturation of liquid iron with FeO and the formation of a separate slag phase occured in all cases, even in the absence of oxygen, as the oxygen pressure of the gas phase, due to the dissociation of sulphur dioxide at pressures of the order used in the present work, is far greater than that of liquid iron saturated with FeO. Thus according to the equation:-

$$2FeO_{(slag)} = 2Fe_{(liq.)} + O_2$$

for which, $\triangle G^{\circ} = 111,250 - 21.67\ T$

$p_{O_2}/$

P_{O_2} @ 1650°C = 1.2×10^{-8}

& P_{O_2} @ 1750°C = 5.4×10^{-8}

whereas, for the dissociation of sulphur dioxide:-

$$SO_2 = \tfrac{1}{2}S_2 + O_2$$

for which, $\Delta G^\circ = 86,525 - 17.25\ T$

P_{O_2} will always be greater than the above values unless the partial pressure of sulphur dioxide is as low as 1.51×10^{-6} at 1650°C. and 4.84×10^{-6} at 1750°C. Thus when $P_{SO_2} = 0.01$ then at 1650°C $P_{O_2} = 4.23 \times 10^{-6}$ atmos. The relationship obtained in the present work between sulphur dioxide and liquid iron, shown in Fig. (18) and expressed mathematically by equation (19) is only applicable when the oxygen pressure of the gas phase is equal to or greater than that of liquid iron saturated with FeO. The corresponding values of P_{SO_2} calculated above for 1650°C and 1750°C are, therefore, the lowest limits for the applicability of equation (19) to the reaction between sulphur dioxide and liquid iron, when oxygen is otherwise absent. If the partial pressure of sulphur dioxide falls below this limit then the liquid iron will not be saturated with FeO, and true equilibrium will be possible, since a free FeO-FeS phase will not form. In such a case the liquid iron will contain more sulphur than that expected according to equation (19). Such conditions, however/

however, are not likely to be met with in practice, since the limiting values of P_{SO_2} and the corresponding sulphur contents of the metal are extremely low. From equation (19) the latter will be:-

at 1650°C $[S]\ \% = 0.612 \times 10^{-4}$

and, at 1750°C $[S]\ \% = 1.676 \times 10^{-4}$

The above deductions are best illustrated on the Fe-O-S ternary diagram, Fig.(25), already referred to above. As was mentioned earlier, the lines A B and A'B', representing the limits of miscibility in the system Fe-O-S at 1750°C and 1650°C respectively, also indicate the "steady state" compositions of the iron phase when it is in contact with sulphur dioxide, the partial pressure of which exceeds the limit given above. Compositions within the areas A B C D and A'B'C D represent equilibrium conditions at 1750°C and 1650°C respectively, when liquid iron is in contact with a sulphur bearing atmosphere whose oxygen pressure lies below that of liquid iron saturated with FeO.

In steelmaking practice the oxygen potential, or partial pressure, of the furnace atmosphere is usually determined by the $CO:CO_2$ ratio of the furnace gases. It has often been stated that the more oxidising the furnace atmosphere, the lower will be the pick-up of sulphur by

the liquid iron from the gases. From the present work, however, it would appear that there exists a limit beyond which any further increase in the oxygen potential of the furnace atmosphere (i.e., decrease in the $CO:CO_2$ ratio) will not decrease sulphur pick-up by liquid iron. This limiting value of the oxygen potential is that which would be in equilibrium with liquid iron saturated with FeO. The $CO:CO_2$ ratio corresponding to this limit was calculated as follows: The saturation of oxygen in liquid iron has been expressed by Taylor and Chipman[21] in the form of the following equation:-

$$\log O\%_{(\text{in liq. iron})} = -\frac{6320}{T} + 2.734$$

Values for different temperatures were substituted in the following equation:-

$$K = \frac{P_{CO_2}}{P_{CO} \cdot [O]}$$

where, $\log K = \frac{7320}{T} - 3.96$

given by Marshall and Chipman[22]. The calculated values of the $CO:CO_2$ ratios are:-

5.06 at 1650°C.

and, 5.35 at 1750°C.

At higher $CO:CO_2$ ratios, liquid iron will absorb more sulphur/

sulphur than the amount calculated from equation (19) whereas lower $CO:CO_2$ ratios, i.e., more oxidising atmospheres, will not result in any less sulphur pick-up than that calculated from the same equation, i.e.,the sulphur pick-up will remain constant below these limiting $CO:CO_2$ ratios. These values, therefore, represent the highest permissible ratios which will result in the least possible sulphur pick-up.

The above conclusions, of course, only apply when direct contact between liquid iron and gas is achieved. The presence of an intermediate slag layer preventing such direct contact would introduce many further complications which cannot be dealt with here.

Conclusions:

The conclusions arrived at in the present work may be summarised as follows:-

1. When the steady state is reached in the reaction between liquid iron and sulphur dioxide, a linear relationship exists between the partial pressure of sulphur dioxide and the sulphur content of the metal.

2. The addition of up to six per cent oxygen to the gas mixture does not alter the above linear relationship.

3. Low temperatures encourage the transfer of sulphur from/

from sulphur dioxide to liquid iron.

4. The relationships in 1-3 may be expressed mathematically as follows:-

$$\log \frac{[S]}{P_{SO_2}} = \frac{2642}{T} + 0.233 \qquad (19)$$

5. Thermal diffusion does not appear to introduce any serious error when using gas mixtures consisting of sulphur dioxide, nitrogen and oxygen.

6. Regarding the system as a whole, equilibrium is not attained, since chemical action between gas and metal would continue until all the iron had been converted into iron oxide and iron sulphide.

7. Of the three reactions by which sulphur dioxide can react with liquid iron:-

(a) $2Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \frac{1}{2}S_2(gas)$

(b) $Fe_{(liq.)} + SO_2 = \underset{(metal)}{FeS} + O_2$

and, (c) $3Fe_{(liq.)} + SO_2 = \underset{(metal)}{2FeO} + \underset{(metal)}{FeS}$

(a) is probably the most rapid and takes place in preference to the other two. (b) is particularly slow. Sulphur probably enters the metal by reaction of the sulphur vapour formed in (a) with the liquid metal, according to the equation:-

$$Fe_{(liq.)} + \tfrac{1}{2}S_2(gas) = \underset{(metal)}{FeS}$$

The/

The sulphur dissolved in the iron approaches equilibrium with the sulphur vapour, but some of the iron sulphide formed is being continuously partitioned into the slag phase along with ferrous oxide formed by reaction (a).

8. There is no rapid mechanism for removal of sulphur from the metal to the gas phase.

9. It is probable that the activity of sulphur is increased by the presence of oxygen in the metal.

10. The boundaries of the region of liquid immiscibility for the temperatures investigated have been established in the ternary system Fe-O-S, and are shown in Fig. (25).

11. It has been shown that the results apply down to a partial pressure of sulphur dioxide of 1.51×10^{-6} atm. at 1650°C. and 4.84×10^{-6} atm. at 1750°C. Below these values the liquid iron will not be saturated with FeO, and the liquid iron will contain more sulphur than that calculated from the expression given above.

12. The highest permissible $CO:CO_2$ ratios which will result in the least possible sulphur pick-up have been calculated to be 5.06 @ 1650°C and 5.35 @ 1750°C. At higher $CO:CO_2$ ratios, liquid iron will absorb more sulphur, but lower ratios will not result in lower sulphur pick-up.

ACKNOWLEDGEMENTS.

This research was carried out under the direction of Professor R. Hay and I wish to record my appreciation for the interest he has unfailingly shown throughout its progress.

I also wish to express my deep gratitude to Dr. P. T. Carter for his valuable help and criticism.

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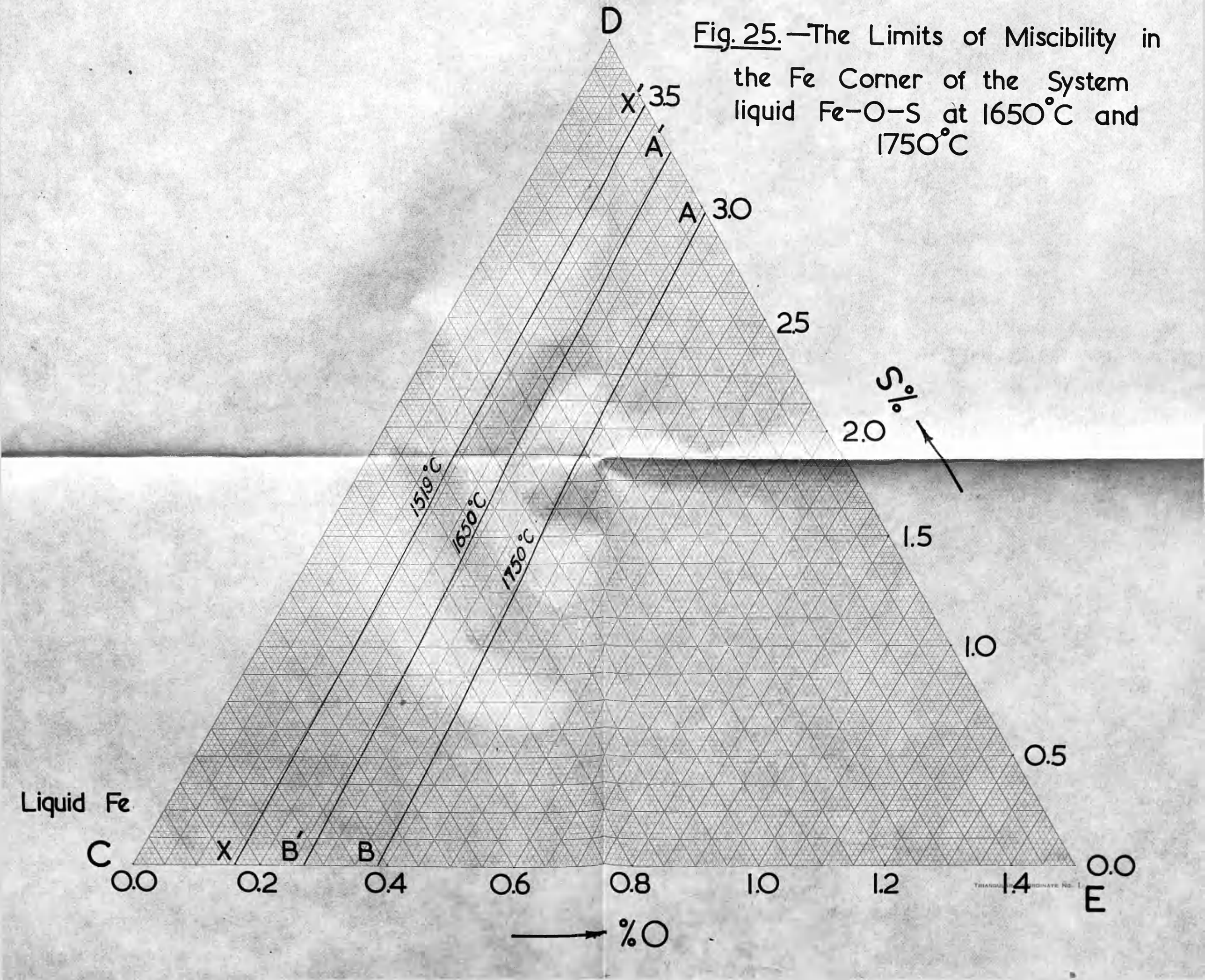

Fig. 25.—The Limits of Miscibility in the Fe Corner of the System liquid Fe–O–S at 1650°C and 1750°C